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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Absorption-spectra of the Rare Earths. By G. H. BAILEY (*Ber.*, 20, 2769—2770).—Krüss and Nilson have recently published (*Abstr.*, 1887, 890) the results of experiments on the absorption-spectra of solutions of certain minerals containing the rare earths; a comparison of various intensities of the absorption-bands observed, induces them to believe in the existence of some 20 new elements. It is here pointed out, firstly, that it is exceedingly difficult to judge the relative intensities of absorption-spectra; and, secondly, that it is impossible to compare, for example, solutions which contain little or no erbium or samarium with those which contain salts of these metals in greater quantity. Thirdly, no consideration is given to the influence of the solvent on the intensity of the absorption-band. On these grounds, the author considers that the evidence brought forward is insufficient to prove the existence of these new elements.

V. H. V.

Action of Light and Reducing Agents on Silver Salts: Formation of Photo-salts. By M. C. LEA (*Amer. J. Sci.*, 33, 349—364, 480—488, 489—494; and 34, 33—36).—It is possible to obtain compounds of silver with chlorine, bromine, and iodine which show varied and beautiful colours, are highly stable except when exposed to light, and can be formed by chemical methods in entire absence of light. These compounds are identical with the substances forming the invisible or latent photographic image, and many of them show a tendency to reproduce colours. The author proposes to call these compounds *photo-salts*, a name which recalls one of their modes of origin without involving any statement as to their chemical nature. They are formed from the normal salts by the action of reducing agents, and contain a lower proportion of the halogen than the normal salts, but their high stability indicates that they are not sub-salts, and do not contain any

free sub-salt. It is most probable that they are compounds of the sub-salts with large proportions of the normal salts, and are analogous in constitution to the "lakes" formed by colouring matters. Their composition varies considerably according to the method of preparation.

Silver Photochloride.—Compounds of silver with chlorine can be obtained with various shades of colour, ranging from white through flesh-colour, pale-pink, rose, copper-red, reddish-purple, and chocolate, to black.

Finely divided metallic silver, obtained by reduction in the wet way, treated for several hours with successive portions of a strong solution of sodium hypochlorite, yields a product which is purple-black, and sometimes even black. If the action is complete, nitric acid of sp. gr. 1.36 removes no silver, the substance, therefore, contains no metallic silver and no subchloride, as the latter would be at once decomposed. Subchloride is at first formed, but is converted into the normal chloride, which at once combines with other subchloride, forming a photo-salt, and thus removing the subchloride from the sphere of action. This process continues until the whole of the silver is converted into a compound of silver subchloride with the normal chloride. Prolonged action of the hypochlorite beyond this point gradually reduces the amount of sub-salt present.

Strong nitric acid destroys all varieties of the photochloride, but the degree of resistance to its action varies widely, and is sometimes very considerable, a fact which is the more remarkable since freshly precipitated subchloride is at once decomposed even by dilute nitric acid.

When protected from light, the photochloride prepared by the above method remains unaltered, even after 18 months. It is far more slowly attacked by ammonia than the normal chloride, several hours being required for complete solution even with a large excess of ammonia. Eventually only metallic silver soluble in nitric acid remains. If the ammonia is poured off shortly before this point is reached, and the undissolved portion is treated with nitric acid, a black residue is left, consisting of metallic silver mixed with a very dark variety of the chloride. This dark variety is insoluble in any acid, and has been mistaken for a passive modification of metallic silver. Some preparations of this dark chloride contained 2.49 per cent. of subchloride, and 97.51 per cent. of the normal chloride.

If a solution of normal silver chloride in ammonia is added to a solution of ferrous sulphate, allowed to remain for one minute, and then mixed with dilute sulphuric acid until strongly acid, the product well washed, boiled with dilute nitric acid, again washed, treated with hydrochloric acid, and finally washed, a brilliant red photochloride is obtained, its colour resembling that of electrolytic copper. The beauty of the preparation depends on the complete removal of metallic silver and of iron compounds. Any silver salt, for instance, the phosphate, will give a similar result.

Silver oxide is heated for a long time at 100°, or is roasted until the colour changes from brown to black, care being taken to avoid absorption of carbonic anhydride, and it is then treated with hydrochloric

acid; or silver carbonate is roasted until black, and then treated with hydrochloric acid. The product has a pale-pink, copper-red, deep red, or burnt carmine colour, according to circumstances.

Ferrous sulphate mixed with excess of potassium hydroxide, then with a solution of a silver salt, and finally with hydrochloric acid, yields a photochloride, the colour of which depends mainly on the amount of reduction. Manganous oxide behaves similarly, but the reducing action is weaker, and must be assisted by heat. Chromous oxide has still less effect, and with cobaltous oxide, reduction is scarcely perceptible without long-continued heating.

Ferric chloride behaves with metallic silver in much the same way as an alkaline hypochlorite, but is less energetic, one or two days being required for a complete reaction. If the action has taken place in the cold, the product is dark purple-black, and contains from 1.52 to 7.5 per cent. of silver subchloride. Prolonged contact with ferric chloride eventually converts the photo-salt into the normal chloride, especially on heating.

When freshly precipitated and moist silver subchloride is treated with nitric acid, there is a brisk effervescence with evolution of nitrogen oxides, but when the substance has been converted into a photochloride by the combination of the normal chloride with the unaltered subchloride, the action ceases. The proportion of subchloride varies from 1.96 to 8.62 per cent., and depends mainly on the strength of the acid and the duration of its action. The colour varies from rose to purple, and is always rendered paler by the removal of silver subchloride by prolonged action of nitric acid, although it by no means follows that the darkest varieties contain the highest proportion of subchloride. With sodium hypochlorite, silver subchloride yields a purple photochloride.

Cupric chloride attacks silver in the same way as ferric chloride, and the action is more energetic, but the removal of copper from the product is difficult. In one case the proportion of subchloride in the photo-salts was 6.28 per cent. If a very dilute solution of silver nitrate is added to cuprous chloride, and the bulky, black powder which is formed is boiled with nitric acid, a red photochloride is obtained.

When a solution of silver chloride in ammonia is added to ferrous chloride, and the greyish or olive-black precipitate is washed with dilute sulphuric acid, it becomes brownish-purple, and the colour is still brighter after treatment with nitric acid. One specimen contained 4.26 per cent. of subchloride.

If hydrogen is passed over silver citrate at 100°, and the product is treated with hydrochloric acid and then with nitric acid, it yields a fine purple photochloride, which in one case contained 3.11 per cent. of subchloride.

A very good method is to act on a silver salt with potassium hydroxide and an organic substance such as lactose, dextrose, gum, tannin, alcohol, &c. The time required varies widely, a few minutes being sufficient with lactose, whilst dextrin requires half an hour. The product is mixed with hydrochloric acid, and after washing is boiled with nitric acid. The best result is obtained if the product is

chestnut-brown after adding hydrochloric acid. At this stage, it contains 92.68 per cent. of silver, and is a mixture of normal chloride, subchloride, and metallic silver. After boiling with nitric acid, it is purple or burnt carmine. One sample obtained with dextrin contained 2.26 per cent. of subchloride; another prepared with lactose contained only 0.34 per cent.

If ferrous sulphate solution is mixed with hydrochloric acid and silver nitrate added, the precipitate is white, but if the silver nitrate is mixed with ammonia in quantity insufficient to neutralise the acid in the iron solution, a photochloride is precipitated which is at first dull purple, but is improved by treatment with hydrochloric and nitric acid.

Potassium ferrous oxalate with silver nitrate yields a black powder which is converted into a deep purple photochloride by treatment first with hydrochloric and then with nitric acid. Ammoniacal silver nitrate with aqueous pyrogallol containing excess of hydrochloric acid gives a grey precipitate, which when washed and treated with hot dilute nitric acid, yields a bright pink photochloride. Silver nitrate mixed with ferrous sulphate yields metallic silver, but if soda or potash is first added, and afterwards hydrochloric acid, red photochloride is obtained. Silver nitrate mixed with excess of sodium carbonate, then added to ferrous sulphate solution, and afterwards treated with hydrochloric acid, yields a photochloride. Photochlorides are also formed when freshly precipitated silver chloride is boiled with finely divided silver and then treated with nitric acid; when the fused normal chloride is partially reduced with zinc and sulphuric acid and treated with nitric acid; when silver is treated with hydrochloric acid mixed with potassium dichromate or permanganate; and when silver is mixed with potassium chloride and chlorate and dilute nitric acid cautiously added.

Photochlorides become purple and purplish-black when exposed to light. With mercuric chloride, they become dirty white; with mercuric nitrate, they dissolve and seem to be decomposed, since they can only be recovered as white normal chloride. Potassium chloride has no effect; with potassium bromide, they become dull lilac; with a small quantity of potassium iodide, they are instantly changed to bluish-grey; with a large quantity, they dissolve somewhat readily, and in time solution is almost complete. Potassium chlorate and hydrochloric acid convert the photochlorides into normal chloride. They show a decided tendency to become red when heated. The change in colour produced by boiling with nitric acid is due to the action of heat, the removal of metallic silver, and the decomposition of uncombined subchloride. It is not possible to dissolve out the normal chloride by means of an alkaline chloride; when boiled with ammonium or sodium chloride, the photochlorides gradually dissolve, a residue of metallic silver being left.

Silver chloride precipitated with excess of hydrochloric acid and exposed to light until it becomes very dark, and then treated with nitric acid of sp. gr. 1.36, yields only a trace of metallic silver. A small quantity of subchloride is formed by the action of light, and combines with the unaltered normal chloride. A small quantity of

metallic silver or of uncombined subchloride is formed at the same time. When a small quantity of the subchloride has been produced, and has formed a photochloride, decomposition ceases.

The brighter coloured varieties of the photochlorides cannot be obtained by the action of light on the normal chloride, but when many silver salts, such as the oxalate, phosphate, tungstate, carbonate, pyrophosphate, and acetate are exposed to light and then treated with hydrochloric acid and with nitric acid, pink, red, and purple products are obtained, which agree in properties with the products of reduction. The photochlorides obtained by different methods are not identical, and vary considerably in their resistance to the action of light, ammonia, and nitric acid. As a rule, the darker varieties are the most stable.

When the rose-coloured photochloride is exposed to the spectrum, it becomes violet in the violet, slate-blue in the blue, is bleached in the green and yellow, and remains unchanged in the red. The maximum effect is near F, and there is a second feeble maximum at the end of the visible violet. With coloured glass, the results are more marked. Under two thicknesses of ruby glass, the colour becomes brighter and redder; under blue, sometimes blue, sometimes grey; under cobalt glass, deep blue; under manganese glass, violet; green and yellow have little effect. The dark varieties of the photochloride do not give such good results as the rose and copper shades. The latter closely resemble the films prepared by Becquerel both in their behaviour to light and when heated, and they are probably identical in composition. The action of light on photochlorides is affected by the presence of other substances, especially such as can give up chlorine. The red chloride darkens in white light, but if mixed with lead chloride, zinc chloride, and certain other chlorides, it bleaches to a considerable extent.

Photobromides are obtained by the same reactions as the chlorides, but the coloured products are not always true photo-salts. Silver bromide with reducing agents sometimes gives a brown form of metallic silver, which when mixed with unaltered bromide resembles a photo-salt in appearance but not in properties. Cold nitric acid dissolves silver from this mixture, but has no action on a photo-salt.

A very fine purple variety is obtained by the action of ferrous hydroxide, but its composition is very variable. One sample contained 7.25 per cent. of subbromide. Six grams of silver nitrate is dissolved in 200 c.c. of water, and ammonia added until the precipitate redissolves; 12 grams of ferrous sulphate is dissolved in 200 c.c. of water, and then mixed with the silver solution and with a solution of 4 grams of sodium hydroxide in 50 c.c. of water. After standing for a few minutes, 5 grams of potassium bromide in a little water is added, and dilute sulphuric acid until strongly acid. The product is washed, and heated cautiously with nitric acid of sp. gr. 1.35 diluted with 5 vols. of water. The photobromide thus obtained has a very fine purple colour, and contains somewhat less than 1 per cent. of subbromide.

Other suitable methods for preparing photobromides are to add an ammoniacal solution of a silver salt to ferrous sulphate and then

treat with hydrobromic acid, or to act on a silver salt with potassium hydroxide and an organic substance and then add hydrobromic acid.

A dilute solution of potassium iodide reduces the colour of the photobromides; a strong solution dissolves them, and yellow normal bromide is precipitated on dilution. Acid ferric sulphate has no action in the cold, but the normal bromide is formed on heating. Ammonia acts more slowly than on the photochlorides. Sodium thiosulphate dissolves the photobromides, leaving a residue of metallic silver. When exposed to light, they darken very much more rapidly than the photochlorides, and the images readily undergo reversal when treated with an ordinary developer. They are much more sensitive than the normal bromide. In the spectrum, the photobromides show little tendency to reproduce colours. Under coloured glass, the results are more marked, but are inferior to those obtained with the photochlorides; they become greenish under blue glass, blue under green, are bleached under yellow, and unchanged under red.

Photoiodides are obtained by methods similar to those employed for the preparation of the photobromides and photochlorides, but are readily decomposed by a slight excess of the alkaline salt. A bright purple variety is obtained by adding iodine to a solution of potassium hydroxide until almost black, diluting with water, and adding gradually to finely divided, reduced silver. The product is then boiled cautiously for a very short time with nitric acid of sp. gr. 1.36 diluted with 12 to 15 vols. of water. Great care is required to avoid conversion of the photoiodide into the normal iodide. Another method is to mix silver nitrate solution with a considerable excess of ammonia, pour the mixture into ferrous sulphate solution, and then add potassium iodide dissolved in dilute sulphuric acid, care being taken to avoid excess of iodide. Excess of silver is removed by means of nitric acid. The proportion of subiodide in the photoiodide varies from 0.64 to 4.63 per cent. The photoiodide cannot be obtained by the action of hydriodic acid on roasted silver oxide.

When normal silver iodide is treated with sodium hypophosphite solution, a brown product is obtained, but the liquid takes up no iodine. It is found, however, that silver iodide can absorb and retain small quantities of free iodine; precipitated silver iodide will in fact decolorise a dilute solution of iodine. This fact explains the gradual disappearance of the invisible or latent images on silver iodide films formed by treating silver with iodising solutions. The silver iodide formed absorbs small quantities of free iodine. When the film is exposed to light, subiodide is formed, and combines with the normal iodide, forming photoiodide, but the free iodine in the film gradually reconverts the photoiodide into normal iodide, and the image is destroyed. This disposes of the last argument in favour of the physical theory as to the nature of the invisible image.

With ammonia, the photoiodides become salmon-coloured, but undergo no further change; there is no separation of metallic silver. Sodium thiosulphate dissolves the photoiodides, leaving a slight residue. Dilute nitric acid mixed with dilute potassium iodide solution converts them into normal iodide. When exposed to light, the photoiodides become greenish-grey, and the image obtained

by development is usually direct, but is occasionally reversed, the photoiodide being intermediate in this respect between the photochloride and photobromide.

Identity of Photo-salts with the Substances forming the Invisible Image.—Sodium hypophosphite has no visible action on silver chloride, bromide, or iodide in the cold, but produces an invisible effect, and renders them sensitive to the action of a developer. If the solution is concentrated, and is heated, brownish-purple protochloride, bromide, or iodide is obtained. Well washed precipitated silver chloride is mixed with a strong solution of sodium hypophosphite and heated for 10 to 15 minutes, then washed and treated with very dilute nitric acid. A pink or reddish-brown product is obtained, which contains 1.77 to 3.53 per cent. of subchloride, and is much more readily attacked by nitric acid than the other varieties of photochloride. By prolonged action of the hypophosphite, silver chloride is reduced to metallic silver.

In the entire absence of light, sodium hypophosphite is able to produce in a sensitive film of a haloid salt of silver a change exactly similar to that produced by light, that is, an invisible image capable of development, and just as light always produces a direct image on silver chloride, but under certain conditions a reversed image on silver bromide, so the hypophosphite always produces a direct image on the chloride, but sometimes a reversed image on the bromide. In both cases, too, prolonged action produces a visible image.

Experiments in this direction are readily made by steeping paper in a solution of soluble chloride or bromide, drying, and then floating on a solution of silver nitrate, washing, and drying. Lines, &c, drawn on such paper with sodium hypophosphite solution are invisible, but can be developed by potassium ferrous oxalate solution or any ordinary developer. The action increases with the time and also with a rise of temperature.

A similar result is obtained with a very dilute solution of potassium hydroxide mixed with lactose or other easily oxidisable organic substance. Both cases are the initial stages of reactions which when prolonged give rise, like the action of light, to the formation of photo-salts.

Chloride, bromide, and iodide paper were exposed to light and then cut in half, one half of each being immersed for five minutes in strong nitric acid, and then washed thoroughly and placed in the same developing solution. The image on the chloride is almost unaffected, that on the bromide has become weaker but is still strong, whilst that on the iodide is completely destroyed. Pieces of the same paper were treated with sodium hypophosphite solution, and one half of each piece immersed in nitric acid. On development, the results were precisely the same as with the images produced by light. The invisible image produced by light is not very materially affected by cold concentrated solutions of potassium chloride or bromide, but is destroyed by a solution of potassium iodide; the invisible image produced by the hypophosphite behaves in exactly the same way.

The action of light on silver chloride always results in a direct image on development, but with the bromide the image gradually becomes weaker as the action of light is prolonged, and eventually the image is reversed, that is to say, the exposed portions of the sensitive film offer greater resistance to the action of the developer than the unexposed portions. Bromide-paper treated with a 20 to 30 per cent. solution of sodium hypophosphite gives a direct image on development, but if a more and more dilute solution is employed, the image becomes weaker and weaker, at last reaching a point at which there is no apparent effect, but with still greater dilutions development gives white marks on a dark ground. The effect is similar to that produced by light, but is in the inverse order.

Sodium hypophosphite reverses the action of light and *vice versa*. If lines are drawn with a concentrated solution of the hypochlorite upon bromide-paper which has been exposed to light, and the paper is then treated with a developer, the lines appear white on a dark ground. If the red or purple photobromide obtained by the action of the hypophosphite or other reducing agent is applied to paper in the form of a film, and exposed to light, and then treated with potassium ferrous oxalate, the exposed portions appear as white upon a dark ground, although before development they were darker than the photobromide. It follows that the photobromide, like the ordinary bromide, is capable of reversal.

When a film of silver tartrate, citrate, benzoate, pyrophosphate, or other stable salt is formed on paper in the usual way, exposed to light under a negative, treated with hydrochloric or hydrobromic acid for some time, well washed, and developed with potassium ferrous oxalate, an image is formed similar to that which would be obtained on a film of chloride or bromide. It follows that one silver salt may be converted into another without losing its property of being reduced when treated with a developer, and it is evident that all such salts must be capable of forming sub-salts. The general existence of such sub-salts has not hitherto been suspected.

After such an image has been treated with hydrochloric or hydrobromic acid, it may be treated with nitric acid until all silver compounds, except the haloid salt, are removed from the paper, but on development the image is brighter and stronger. It follows that the product of the action of hydrochloric or hydrobromic acid on the exposed silver tartrate, citrate, &c., is identical with the product of the direct action of light on silver bromide or chloride. If paper prepared with silver tartrate, oxalate, &c., is exposed to light, part of it treated in the dark with hydrochloric or hydrobromic acid, washed with nitric acid, and afterwards developed, the portions treated with the haloid acids give a black image, whilst the other portions remain white, a fact which shows that the sub-salts of the tartrate, oxalate, &c., are soluble in nitric acid. When the tartrate or oxalate paper is exposed to light for a short time, marked with hydrochloric or hydrobromic acid and treated with a developer, the marks develop first, and hence the subchloride or subbromide is more susceptible to the action of the developer than the subtartrate or suboxalate. The greater sensitiveness of the haloid salts may be due to their power of

combining with their own sub-salts, so that the reduction which begins with the sub-salt quickly extends to the normal salt with which it is combined. Other silver salts have not this power, and therefore are more slowly and irregularly attacked by developing solutions.

When paper prepared with silver tartrate, oxalate, &c., is exposed to light, treated with hydrochloric acid and developed, the effect of a short exposure is the same as that of a long exposure. A short exposure produces sufficient alteration to serve as a nucleus for development; a long exposure does no more. C. H. B.

Spectrum Researches on the Energy of the Action of Bromine on Aromatic Hydrocarbons. By J. SCHRAMM and I. ZAKRZEWSKI (*Monatsh.*, 8, 299—309).—Sunlight was reflected through a vertical slit by a heliostat on to a condensing lens of great focal length. By means of a bisulphide of carbon prism, a spectrum 30 cm. long was produced, in which Fraunhofer's lines were distinctly visible. Nine test-tubes were fastened at equal distances between the lines B and H, since preliminary experiments showed that the chemical action was confined to the space between these lines. A few drops of bromine were added to the solution of the carbon-compound, and the mixture was equally distributed among the test-tubes. The time occupied from first illumination to total disappearance of the bromine was observed in each tube. To exhibit graphically the energy of the reaction, curves are plotted, so that the abscissæ indicate the part of the spectrum and the ordinates the reciprocals of the duration of the reaction. In this way experiments were made on toluene, ethylbenzene, and metaxylene. All the researches showed that the maximum action takes place in the yellow or yellow-green. The blue and violet rays exert a slight action, and the dark-red scarcely any at all. The curves are therefore similar in character to that for the intensity of light in the spectrum. C. S.

Increase of Photo-electric Currents. By J. MOSER (*Monatsh.*, 8, 373).—The author finds that the electromotive force produced by the action of sunlight on chloride, iodide, or bromide of silver plates can be considerably increased by immersing them in a bath of a dye, say, erythrosin. C. S.

Electric Properties of Rock-salt. By F. BRAUN (*Ann. Phys. Chem.* [2], 31, 855—872).—Although this substance is isotropic as regards light, its modulus of elasticity according to Voigt is 4170, 3400, and 3180 kilo. per sq. cm. in directions parallel respectively to normals to the cubical, dodecahedral, and octahedral faces. On Maxwell's theory, high insulating properties might be expected in it, since it is highly diathermanous. It is in fact so good an insulator, although not perfect, that its dielectric constants could be well determined.

Much of the paper is devoted to describing the methods of determining the constants of the instruments used. The ends of a rock-salt column were cut parallel to cubical faces, a hole drilled length-

wise nearly through its axis, and the vertical edges planed away until the section of the column was octahedral. Alternate faces were then cubical and dodecahedral. Plates of tinfoil were attached to two of these, and, the inner chamber being filled with mercury charged to a high potential, the charges on these were compared by the electrometer. Within the limits of experimental error, the charges were found to be equal. Similar experiments with two little condensers constructed from plates parallel to cubical and octahedral faces showed the dielectric constants of these also to be the same. Absolute measurements were not made.

The conductivity was also measured by the electrometer. One plate of a little rock-salt condenser was joined to a battery of 16 large Leyden jars, the potential of which (1500 to 3000 volts) was observed from time to time, so as to calculate the rate at which its charge was dissipated through leakage. The other plate being joined to the electrometer, the indications of the latter afforded a measure of the conductivity. The method is fully described: the results are as follows (specific resistance of mercury = 1).

Specific resistance perpendicular to cubical face = 1.33×10^{21} .
 „ „ „ octahedral face = 2.63×10^{21} .

Ratio of resistance perpendicular to cubical face to resistance perpendicular to dodecahedral face = 3 : 2.

Specific resistance of paraffin = 3.02×10^{22} .

The dielectric constants were also found to be independent of the time of electrification.

The provisional conclusion is, that rock-salt is dielectrically isotropic, but anisotropic as regards conductivity. Ch. B.

Validity of Joule's Law for Electrolytes. By H. JAHN (*Ann. Chem. Phys.* [2], 31, 925—940; see also *ibid.*, 25, 49).—The object of these experiments was to ascertain whether the portion of the current energy expended on polarisation during electrolysis contributes to the development of heat or not. The method of inquiry consisted in measuring the heat developed during the electrolysis of antimony chloride between antimony electrodes, in a cell enclosed in a Bunsen's ice-calorimeter, and the current flowing through the circuit, and calculating Joule's constant a from the equation—

$$W_{\text{e}} = aJ(iR - J\rho),$$

where W = heat developed per second in the calorimeter, iR = difference of potential between two points in the circuit including the cells, ρ = resistance of the part of the intervening circuit not included in the cell, and J = strength of current. Antimony chloride was selected on account of the high polarisation generated during its electrolysis.

Since antimony separates from its chloride sometimes in the ordinary form, sometimes in the explosive form, experiments were made with electrodes of both kinds. During the rapid rise of the polarisation (about five minutes) the strength of the current E was assumed to vary according to the law $E = E_0 + at + bt^2$. The total

current was then determined by summation from observations at intervals of five minutes. From various experiments it was found,

$$a = 0.2367; 0.2362; 0.2375; 0.2376; 0.2383; 0.2382.$$

The author shows that if the polarisation energy did not contribute to heat development the result should have been $a = 0.2693$.

Ch. B.

Conductivity of Pure Water, and its Temperature Coefficients. By E. PFEIFFER (*Ann. Phys. Chem.* [2], **31**, 831—855).—This paper refers chiefly to the conductivity of water contained in glass vessels, and hence rendered more or less impure by dissolution of the glass substance. Kohlrausch's method was used. One of the electrolytic cells has been already described (*ibid.*, **25**, 232). A second form consisted of two platinum plates (3 cm. square) held at a fixed distance apart by glass rods fused to their faces, and suspended by the conducting wires in a glass vessel. Since the conductivity changes rapidly from the moment of filling, observations were made at regular intervals, and the initial conductivity calculated by extrapolation.

The solvent action on glass is always apparent, but increases greatly with the temperature. When successive charges of water are poured into a new glass vessel, the resulting time-rate of increase of conductivity is at first rapid, but after a time reaches a nearly constant minimum value which does not change for months. When the same mass of water is allowed to remain in a glass vessel at constant temperature for a long time, the time-rate of increase of conductivity grows gradually greater; from this the author concludes that the conductivity is not proportional to the amount of dissolved glass substance. He thinks that the suitability of different kinds of glass for chemical purposes might be usefully tested in this way.

The rapid fall in conductivity which takes place immediately after filling (Kohlrausch, *Ann. Phys. Chem.* [5], **26**, 220; Pfeiffer, *Abstr.*, 1886, 115) is attributable to the diffusion into the fresh liquid of a layer of the previous charge adhering to the glass and electrodes.

Temperature coefficients have been investigated by Kohlrausch, Vicentini, and Arrhenius. For different solutions, these tend towards equality with increasing dilution; for a particular electrolyte, the coefficient is nearly constant for highly dilute solutions of different strengths; for an excessively dilute solution, it at first decreases as the strength increases. Owing to the constantly changing strength of the solution, its determination for the particular electrolyte furnished by the soluble part of the containing glass vessel was laborious. The results are given in lengthy tables. The initial conductivity of the purest water used was $\lambda = 0.65$ ($\lambda = k_{18} \times 10^{10}$) at 14° ; and observations were continued until λ about equalled 20. Curves were then constructed showing the variations of the temperature coefficients $\alpha = \Delta\lambda/\lambda_{18}$. In one vessel, neglecting minor variations, as λ increased from unity α diminished to a minimum 0.024 at $\lambda = 3$, then increased to a maximum 0.0269 at $\lambda = 5$, and from $\lambda = 6$ onwards became constant at 0.026. In the second vessel (presumably of a different kind of glass), α reached a minimum for $\lambda = 2$, a maximum for $\lambda = 3.5$, and became constant at 0.023 when $\lambda = 6$. For water

which had previously remained for some time in a third vessel, the variations were similar, and α became constant when $\lambda = 9$. The initial variations amounted to about 12 per cent.

The law that the coefficient is constant for very dilute solutions appears to hold only so long as the electrolyte exceeds in amount the impurities (possibly organic) originally contained in the water.

Ch. B.

Formation of Hydrogen Peroxide at the Anode during the Electrolysis of dilute Sulphuric Acid. By F. RICHARZ (*Ann. Phys. Chem.* [2], **31**, 912—924; see also Abstr., 1885, 624, and McLeod, *Trans.*, 1886, 591).—The author has repeated some of Berthelot's experiments (Abstr., 1878, 372; 1886, 607) on this subject, and in the main confirms his results. Sulphuric acid of 70 per cent. appears to be most suitable for developing hydrogen peroxide by electrolysis. In a 40 per cent. solution, persulphuric acid alone is formed. As a test for hydrogen peroxide in presence of persulphuric acid, the author recommends a solution of titanous acid in sulphuric acid. This gives an intensely yellow precipitate, which decolorises the same amount of permanganate as the peroxide which goes to form it. The peroxide may be estimated by permanganate in presence of persulphuric acid; and the latter subsequently estimated by adding ferrous sulphate in excess, and titrating back with permanganate.

Theories have been proposed by Hoppe-Seyler (*Zeit. physiol. Chem.*, **2**, 25) and Traube (Abstr., 1886, 660), who have shown that hydrogen peroxide can be formed at the cathode by reduction of molecular oxygen. The author accounts for its appearance at the anode. When a solution containing only sulphuric and persulphuric acids is allowed to remain, the latter gradually disappears, and hydrogen peroxide is at the same time formed. The author has studied this reaction quantitatively, but does not confirm Berthelot's statement that as decomposition goes on the ratio of hydrogen peroxide to persulphuric acid tends to become 2. In a dilute sulphuric acid solution, the decomposition is very slow, but it is greatly accelerated by adding strong sulphuric acid; from this the author concludes that the appearance of hydrogen peroxide at the anode in a strongly acid solution is always the result of this purely chemical reaction. Contact with a platinum plate almost entirely prevents the formation of hydrogen peroxide in a 40 per cent. sulphuric acid solution, although by catalysis it hastens the disappearance of persulphuric acid; especially when the platinum has been ignited, and consequently become charged with flame gases.

When a 68 per cent. acid solution is electrolysed by a current of 1.1 amperes, the quantity of hydrogen peroxide increases for about three hours, and then becomes stationary. The persulphuric acid, however, goes on increasing. On breaking the current, the peroxide at first noticeably increases, but the persulphuric acid rapidly disappears.

The fact that water is under certain circumstances oxidised by active oxygen, in conjunction with the fact that the peroxide is not directly formed at the anode during electrolysis, is a proof that the molecules of water cannot be electrolysed. The real anion is SO_4 ,

and from this oxygen can only be liberated as O_2 or O_3 . Traube supposes that peroxides which contain an even number of oxygen-atoms can alone form H_2O_2 ; and that those formed at the positive pole during electrolysis, and which contain an uneven number of such atoms, cannot form H_2O_2 . The decomposition of persulphuric acid clearly contradicts this latter view.

CH. B.

Electromotive Dilution Constants. By J. MIESLER (*Monatsh.* 8, 365—372).—The electromotive force of polarisation alone was measured at the beginning and end of each experiment (to test its constancy) by means of a Siemens' universal galvanometer and a capillary electrometer. Next the concentration cell was introduced, so that the electromotive force due to difference of concentration aided or opposed the electromotive force of polarisation. By subtracting or adding the electromotive force of polarisation, the electromotive force due to differences of concentration was determined from the observed total electromotive force. Thus the following values of dilution constants in millivolts were obtained:—

	Acetate.	Sulphate.	Nitrate.	Chloride.	Bromide.	Iodide.
Cadmium .	1·5	2·8	—	—	—	—
Copper ...	2·3	3·6	—	—	—	—
Lead	2·6	—	8·3	—	—	—
Zinc.....	5·9	—	11·6	13·4	11·9	10·4
Silver.....	10·7	12·0	16·2	—	—	—

Taking any two rows in the table, it will be seen that the numbers in corresponding columns have a constant difference (Moser's law), whilst in the case of the three haloid salts of zinc the differences of values of the dilution constants have an obvious relation to the atomic weights of the halogens.

C. S.

Influence of Ultra-violet Light on the Electric Discharge. By H. HERTZ (*Ann. Phys. Chem.* [2]. 31, 983—1000).—The author has discovered that ultra-violet radiation favours the electric discharge between two conductors in a remarkable way. As sources of such radiation, the sun, burning magnesium, or even ordinary flame, may be used; but by far the most effective are the electric arc and an induced electric discharge. To produce the phenomenon, the primary circuits of two induction coils, a large one (10 cm.) and a smaller one (1 cm.), are joined in circuit with the same battery (six Bunsens) and interruptor. Perfect synchronism in the induced discharge is thus secured. The terminals of the large coil being arranged to give a good spark 1 cm. in length, the two coils are placed close together, and an opaque screen interposed. The terminals of the small coil are then drawn apart until sparks just cease to pass. On now removing the screen the discharge is re-established.

The author describes many experiments to test the nature of the effect. The influence is not electrical, since non-conducting screens

are effective as well as metal plates. It varies in some inverse ratio with the distance, and is distinctly produced when the coils are 1 m. apart. In the above experiment, the larger spark may be either short and dense, or long and zig-zag, and every part of it is effective. The smaller spark, however, should be short (between knobs); the seat of the action upon it appears to be in the neighbourhood of the cathode or negative pole. The influence is reciprocal; that is, the smaller spark also favours the larger. The action is propagated in straight lines, like light, and may be reflected from polished surfaces. It may also undergo refraction; but its refrangibility (roughly measured by means of a quartz prism) is much greater than that of the violet rays. Most solid substances are opaque to it; amongst these glass, paper, agate, and mica, even in the thinnest sheets, are noticeable. Amongst crystalline substances, copper sulphate, topaz, and amethyst are opaque to it; but it is transmitted by sugar, alum, calc-spar, and rock-salt; transparent gypsum and rock crystal transmit it perfectly. Amongst liquids, water transmits it freely; sulphuric and hydrochloric acids, alcohol, and ether, less so; whilst melted paraffin and petroleum, benzene, bisulphide of carbon, ammonium hydro-sulphide, and coloured liquids generally, stop it completely. Solutions of potassium, sodium, and magnesium sulphates, are fairly transparent to it; those of mercuric nitrate, sodium thiosulphate, potassium bromide and iodide, are very opaque. Amongst gases, air, hydrogen, and carbonic anhydride are very transparent; chlorine, and bromine and iodine vapours, partially so; and coal-gas and nitric peroxide very opaque.

Even an ordinary candle-flame may produce effects similar to those described, and may cause the reappearance of sparks between the terminals of an induction-coil after they have been drawn so far apart that the discharge has ceased. Similar effects are produced by the luminous flames of gas, wood, and benzene, and the non-luminous flames of alcohol, carbon bisulphide, and the Bunsen burner. Incandescent platinum, and the flames of sodium, potassium, sulphur, and phosphorus, and of pure hydrogen, are without effect. The effective rays are more refrangible even than the so-called photographic rays; for the latter are not sensibly absorbed by coal-gas.

CH. B.

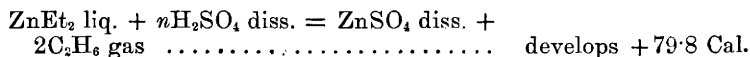
Specific Heat of Liquid Carbon Compounds. By R. SCHIFF (*Gazzetta*, 17, 286—303).—In a former memoir (Abstr., 1887, 7), the author has shown that the variation of the specific heats in a homologous series of compounds is expressible either by a straight line, or a small number of parallel lines. In the equation for the mean specific heat $C_{t-p} = a + b_{(t+p)}$, the coefficient b remains constant for all the terms of a homologous series, whilst the coefficient a either remains constant for all or several terms of the series, or varies *per saltum* with the molecular weight. These conclusions are confirmed in the present memoir, in which determinations are given of the specific heats of the ethereal salts of the chloro-substituted acetic acids and of the succinic acids, as also of certain aromatic compounds. The specific heats of ethereal salts of the propyl and allyl series are also compared. Thus it will be seen in the table below that the value

for *b* in all the ethereal salts of mono-, di-, and tri-chloroacetic acid is a constant = 0·00038, in those of the succinic acids = 0·00066, in aniline and toluidine = 0·0007. Further, the value for *a* in the allyl salts of propionic, butyric, and valeric acids is a constant = 0·433, but in other cases it varies somewhat indefinitely. From these results, the author concludes that neither isomerism nor change of molecular weight produces definite variations in the specific heats.

	<i>a.</i>	<i>b.</i>
Methyl chloracetate.....	0·3747	0·00038
Ethyl ".....	0·39	"
Propyl ".....	0·4067	"
Allyl ".....	0·3888	"
Methyl dichloracetate.....	0·3032	"
Ethyl ".....	0·3215	"
Propyl ".....	0·3335	"
Allyl ".....	0·3244	"
Methyl trichloracetate.....	0·2592	"
Ethyl ".....	0·2778	"
Propyl ".....	0·2892	"
Allyl ".....	0·2806	"
Allyl acetate.....	0·4305	0·00088
Isobutyl acetate.....	"	"
Allyl propionate.....	0·433	"
" butyrate.....	"	"
" valerate.....	"	"
" benzoate.....	0·3732	0·00075
Ethyl oxalate.....	0·4199	0·00066
Propyl ".....		
Ethyl malonate.....		
Propyl ".....		
Allyl oxalate.....	0·4122	"
Isobutyl oxalate.....	0·4274	"
Isoamyl ".....	0·4354	"
Ethyl succinate.....	0·4391	"
Propyl ".....		
Allyl ".....	0·4323	"
Isobutyl succinate.....	0·4421	"
Isoamyl ".....	0·4493	"
Aniline.....	0·4706	0·00070
Orthotoluidine.....		
Dimethylaniline.....	0·4018	0·00092
Diethylaniline.....	0·4343	"
Chlorobenzene.....	0·2988	0·00074
Chlorotoluene.....	0·316	"
Benzyl chloride.....	0·3225	"

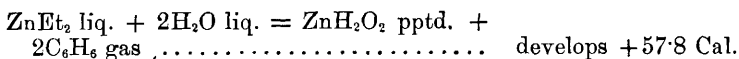
V. H. V.

Heat of Formation of Zinc Ethyl. By GUNTZ (*Compt. rend.*, 105, 673—674).—The zinc ethyl was decomposed by dilute sulphuric acid—

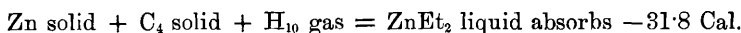
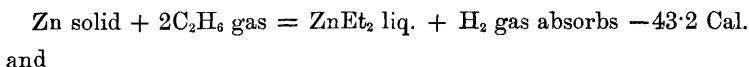


With hydrochloric acid, the number obtained is +78.0 Cal., but when these numbers are corrected for the heats of dissolution of the zinc salt in the excess of acid they become +80.8 and 77.8 respectively.

Taking the mean of these values, it follows that—



the great development of heat explaining the rapidity with which this decomposition takes place. Further—



The formation of zinc ethyl from its elements or from zinc and the hydrocarbon is accompanied by a very considerable absorption of heat.

C. H. B.

Relation of Gases to the Laws of Marriotte and Gay-Lussac.

By C. PUSCHL (*Monatsh.*, 8, 327—337).—If $a = \frac{1}{v} \frac{dv}{dt}$ be the coefficient of expansion, and $c = -\frac{1}{v} \frac{dv}{dp}$ the compressibility, we have—

$$\frac{d(pv)}{dp} = v(1 - cp) = h \text{ say.}$$

When $h = 0$, Marriotte's law holds, and the gas will be more or less compressible than the law requires, as h is greater or less than 0.

For a gas at the critical temperature and compressed from an ordinary density, pv diminishes with the pressure, and h is therefore negative. As the pressure approaches the critical pressure, h diminishes and ultimately $= -\infty$. Further compression causes h to increase, and for a certain pressure $h = 0$. Here Marriotte's law holds. For greater pressures h is greater than zero, and the departure from Marriotte's law is in the reverse direction.

When the temperature of the gas is higher than the critical, h reaches a finite minimum during compression. This minimum increases with the temperature, and for a certain temperature the minimum value of h will be zero, and then both $h = 0$, $\frac{dh}{dp} = 0$. At still higher temperatures the minimum value of h will be positive, and pv will continually increase, as happens for example in the case of hydrogen. It appears therefore that the temperature for which $h = 0$, $\frac{dh}{dp} = 0$ simultaneously is the highest possible at which Marriotte's law can be exactly obeyed. The present method of consideration also shows that at a sufficiently low temperature hydrogen behaves like ordinary gases.

If we trace a curve with ordinate h and abscissa p , there will be a point on it for which h is a minimum. This point will lie above or below

the axis of abscissæ, according as the temperature exceeds or falls short of that for which $h = 0$, $\frac{dh}{dp} = 0$. For the lower temperatures, the curve meets the axis in two points. At the point with the smaller abscissa, pv is a maximum for $\frac{d(pv)}{dp} = h = 0$, and also $\frac{dh}{dp}$ is negative. At the other point pv is similarly a minimum. Consequently for all gases a maximum value of pv will precede a minimum, and at a certain temperature above the critical temperature the two will coincide.

Again, when $h = 0$ and $\frac{dh}{dp} = 0$, we have—

$$\frac{dh}{dt} = pv \frac{da}{dp}.$$

If, however, Marriotte's law be exactly obeyed—

$$\frac{dh}{dp} dp + \frac{dh}{dt} dt = 0,$$

and thus

$$\frac{dh}{dp} dp + pv \frac{da}{dp} dt = 0.$$

Since $\frac{dh}{dt}$ is positive, so also is $\frac{da}{dp}$, and for positive values of $\frac{dh}{dp}$, and for minimum values of pv , the pressure increases as the temperature diminishes. Since Amagat found in the case of oxygen the pressure at the minimum of pv decreases with rise of temperature, we infer this gas was nearly at that temperature where the maximum and minimum of pv coincide.

Similar reasoning is applied to the consideration of Gay-Lussac's law, and results of a very similar nature are deduced. C. S.

Highest Boiling Point of Fluids. By C. PUSCHL (*Monatsh.*, 8, 328—341).—A gas or fluid can be reduced to such a condition that v being its specific volume, p its pressure,

$$\frac{dp}{dv} = 0 \text{ and } \frac{d^2p}{dv^2} = 0,$$

or putting $e = -v \frac{dp}{dv}$,

$$e = 0 \text{ and } \frac{de}{dv} = 0.$$

Thus the zero value of e is a minimum for the critical state. If the temperature is lowered, the minimum value of e reached during compression is negative, and there must therefore be for every temperature two values of v , for which $e = 0$. At the greater value of v , $\frac{de}{dv}$ is positive, and p is a maximum, whilst the contrary holds for the less value. When the volume is greater than that for the maximum

of p , the substance exists in the form of vapour, and when the volume is less than that for the minimum value, the substance is fluid. Between the two, the substance is in an unstable state.

A saturated vapour may be compressed, so that e changes from a positive value to zero, and then the tension is a maximum $= p'$. And in a similar manner, by sufficiently reducing the pressure on a fluid, the tension may be made a minimum $= p''$. For tensions $< p''$, the fluid will be in an unstable condition.

Suppose that a substance at a temperature above the critical fills a rigid vessel of such volume that the substance is of the critical density. If the temperature be lowered, $\frac{dp}{dt}$ will be positive. Thus

whilst at the critical temperature the vapour-tension $p = p''$, at a lower temperature p is $< p''$. But in accordance with what precedes, the fluid and its vapour are now in unstable equilibrium. Also p'' at a sufficiently low temperature is negative. Thus there must exist a temperature somewhere below the critical when p again $= p''$. At this point, when the temperature is lowered, the substance suddenly appears liquid, and on the other hand with rise of temperature, it completely changes into vapour. This temperature is therefore defined to be the highest boiling point of the liquid. If the mass contained in the vessel be greater or less, the temperature of the highest boiling point will not be affected.

C. S.

The Relation of Hydrogen to Marriotte's Law. By C. PUSCHL (*Monatsh.*, 8, 374—377).—As in his previous papers, the author traces the increase or decrease of the quantities, a , the coefficient of expansion, apv and h , by considering the signs of their differential coefficients. Since, according to Regnault's experiments, not only pv but also h increases as the pressure increases up to 20 m., he concludes that in order that h may have a minimum at greater compression, it must have first a maximum at a pressure above 20 mm. If hydrogen be allowed to expand, h will diminish, and we may conjecture that when the pressure is sufficiently small, h will be equal to zero. In this case, pv is a minimum. Since $\frac{dh}{dt}$ is positive, this minimum value will occur

at greater pressures for diminishing temperature. In gases for which pv reaches a maximum through rarefaction, a minimum will occur on further rarefaction, and with diminishing temperature the maximum and minimum will approach towards coincidence.

C. S.

Evaporation and Dissociation; Continuous Changes from the Gaseous to the Liquid State at all Temperatures. By W. RAMSAY and S. YOUNG (*Phil. Mag.* [5], 24, 196—212).—A further proof of the correctness of the formula $p = bT - a$ (where p is the pressure, b and a are constants for each separate volume of 1 gram, and T is the absolute temperature), is furnished by the behaviour of methyl and ethyl alcohols, under a very wide range of temperature, pressure, and volume. Tables are given showing the correspondence of numbers calculated by the above formula with those experimentally determined.

The expression bT is equivalent to the first term of Clausius's and Van der Waals' formulæ, $\frac{RT}{(v-\beta)}$, but it is by no means so simple. It would appear that b is not any simple function of the volume of the gaseous or liquid matter; and we are still in ignorance of the true relations between volume on the one hand, and pressure and temperature on the other. With constant volume, however, temperature and pressure have the simple relation already mentioned.

The behaviour of acetic acid was also investigated, and the data furnished by E. and L. Natanson (Abstr., 1886, 657) for nitric peroxide were also made use of. These two substances exhibit a behaviour markedly different from that of stable bodies. For whereas the isochoric lines (or lines of equi-volume) are straight with stable substances, when mapped against temperature and pressure as ordinates and abscissæ, those of acetic acid and nitric peroxide are curves of double flexure, tending at higher temperatures and pressures to become tangential to isochoric lines, calculated on the theoretical assumption that acetic acid and nitric peroxide have respectively the simpler formulæ $C_2H_4O_2$ and NO_2 ; and at lower temperatures and pressures approaching, as if they would ultimately touch, the theoretical isochoric lines of the more complex molecules $C_4H_6O_4$ and N_2O_4 . The gradual dissociation of these molecules is thus traced, and these substances show and exhibit no analogy with stable substances. It cannot therefore now be asserted that the abnormal vapour-density of these compounds is ascribable to the same cause as the high vapour-density of stable substances at high temperatures and correspondingly high pressures.

The paper also shows the deviation from Boyle's and Gay-Lussac's laws exhibited by ether. It is to be noted that at any given volume smaller than 300 c.c. per gram, the pressure of vapour is below what is calculable on the assumption that ether gas is "perfect." At greater volumes, this divergence is barely noticeable by experiment. Keeping the volume constant, if the temperature and consequently the pressure be raised, there is a continually decreasing difference between the found and what may be called the "theoretical" pressure. At a certain sufficiently high temperature, the found and "theoretical" pressures are identical. At a still higher temperature, the "theoretical" pressure is below the found pressure. The physical meaning of this fact appears to be as follows:—The pressure of a gas depends on the number of molecules present in unit volume, on the average velocity of each molecule, and on the number of impacts on unit area of the surface of the containing vessel in unit time. With constant volume, since the mean distance between the molecules remains constant (on the assumption that the individual molecules are incompressible), the cohesion of the molecules is assumed to be constant. But the rise of pressure produced by rise of temperature of a theoretical gas is based on the assumption that each impact takes place at the centre of each molecule; that is, that the actual volume of the molecules themselves is *nil*. But as this is not the case, as impacts must take place at some distance from the centres of the molecules, they must necessarily be more frequent. The effect of cohesion is to reduce the pressure of the gas, by reducing the average velocity of the molecules, and this, for

any given volume, by a constant amount. Hence below a certain temperature the pressure will be less than that of a normal gas, and if the temperature be reduced sufficiently, will become negative. With rise of temperature the average velocity of each molecule will increase at the same rate as in the case of a perfect gas, but the number of impacts, owing to the increased chances of collision, and consequently the pressure, will increase at a greater rate than if the gas were perfect. Hence a temperature will ultimately be reached when the pressure will be as much decreased by cohesion as it is increased by the more frequent encounters of the molecules; and at that temperature the density of the gas will be normal. At still higher temperatures, the pressure, and therefore the value of the expression pt/v , will be greater, and the vapour-density less than that of a perfect gas. That the numerical value of the expression pt/v would ultimately exceed unity has indeed been experimentally proved by Natterer, in his experiments on the compression of the so-called permanent gases, at temperatures far above their critical points.

In conclusion, it is pointed out that the equations of Clausius, van der Waals, and Sarrau do not express the true relation between volume, temperature, and pressure. As before stated, the relation of temperature and pressure to volume is by no means so simple as they represent it to be.

W. R.

Compressibility of Solutions of Gases. By F. ISAMBERT (*Compt. rend.*, **105**, 375—377).—All known facts indicate that the solution of a gas in a liquid is a very complex phenomenon, and these experiments were undertaken with a view to throw some light on the problem of the nature of solution. The coefficients of compressibility obtained were as follows:—

Water : -0.0000443 at 20° .

Ammonia (330 litres of gas per litre of liquid) : -0.0000381 at $21-22.5^{\circ}$.

Ammonia (140 litres of gas per litre of liquid) : -0.0000389 at $20.4-22.2^{\circ}$.

Hydrochloric acid (at 22°) : -0.0000366 at $19.6-20.5^{\circ}$.

Alcohol : -0.0001076 at 19° .

Ammonia in alcohol (87 litres per litre) : -0.0001071 at $18.0-19.7^{\circ}$.

Sulphurous anhydride in alcohol (60 litres of gas per litre of solution) : -0.0001031 at $18.9-20.3^{\circ}$.

Ether : -0.000183 at 21.5° .

Ammonia in ether : -0.000185 at $21-22^{\circ}$.

The solution of hydrogen chloride, which is usually regarded as containing definite hydrates, has a compressibility less than that of water, and in this respect resembles saline solutions. An aqueous solution of ammonia behaves in the same manner. The volume of ammonia dissolved by ether is too small for any conclusion to be drawn from this case, whilst the compressibility of the solution of ammonia in alcohol is practically identical with that of alcohol, and that of sulphurous anhydride in alcohol is slightly lower. The mere dissolution of a gas in a liquid has very little effect on the compressibility of

the latter. An aqueous solution of ammonia, however, behaves like a true compound. C. H. B.

Solution. By W. DUREHAM (*Chem. News*, **56**, 152—153).—In this paper the author draws attention to the support the theory, promulgated by him in 1878, receives from the thermochemical results accumulated of late years. According to this theory, dissolution of a substance in a liquid is due to the chemical affinity of the elements of the substance dissolved for the elements of the solvent, hence common salt dissolves in water, on account of the affinity of sodium for oxygen and chlorine for hydrogen; further chemical affinity is not exhausted in all cases of chemical combination, but sometimes sufficient affinity remains to form "solution compounds."

In support of these statements, he points out that as regards chlorides, bromides, iodides, sulphates and nitrates, the available data indicate that the heat of dissolution varies directly; firstly, as the heat of combination of the positive element of the salt with oxygen in water varies; secondly, as the heat of combination of the negative element with the hydrogen varies; but that it varies inversely as the heat of combination of the positive and negative elements of the salt varies. Moreover, when salts differing in heats of combination are dissolved, the heats of dissolution differ to a similar extent, the greatest heat of dissolution being associated with the lowest heat of combination.

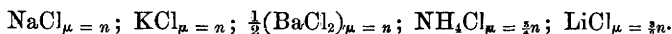
The author shows that the absolute amount of heat of dissolution appears to arise from a balancing of affinities among the constituent elements, for instance, when $M, Cl_2 - [M, O, Aq + Neutr.] = H_2, Cl_2, Aq - H_2, O$ there is no heat of dissolution, and the salt is not soluble. It also would appear that, in neutralising an oxide by an acid solution, the operation is incomplete as long as the salt remains in solution; positive heat of dissolution indicating that the oxide and acid are not completely decomposed, whilst negative heat would indicate that the salt and water, resulting from the double decomposition, are not completely formed. When both parts are complete there is insolubility. In the case of sulphates, when the heat of combination of the oxide with the sulphuric anhydride is equal to the heat of combination of the metal with sulphur, there is insolubility, but when the former is less than the latter solubility appears. Examples are given in the original paper illustrating all the above statements and deductions. The author suggests that dissolution is probably a periodic function of the elements. D. A. L.

Solution. By S. U. PICKERING (*Chem. News*, **56**, 181—182).—The author, commenting on Durham's paper (preceding Abstract), complains of his (Durham's) reasoning in a circle when drawing his conclusions from the thermochemical data. Moreover, the author warns those in search of laws in thermochemistry as to the uncertainty attached to experimental numbers which agree absolutely with or come even within 100 cal. of the theoretical. D. A. L.

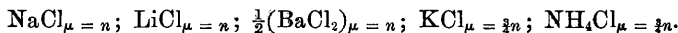
Nature of Solution. By S. U. PICKERING (*Chem. News*, **56**, 191—192).—Referring to a recent communication by Nicol (*ibid.*, p. 162), the author states that the hypothesis on which Nicol bases his argument of the vapour-pressures being a measure of the heat of dissolution is a pure assumption, and one for which we have no particle of evidence.

In a few subsequent remarks, he endeavours to clear up some of the points in dispute between himself and Nicol. D. A. L.

Salt Solutions. By C. BENDER (*Ann. Phys. Chem.* [2], **31**, 872—888).—The author describes further experiments on “corresponding” solutions (Abstr., 1885, 12). Tables are given showing the volumes, densities, and coefficients of expansion of solutions containing from 1 to 6 gram-molecules, or half-molecules, of lithium, ammonium, and barium chlorides per litre. By the aid of these and previous tables, the author has determined by trial the strengths of solutions which, when mixed in equal volumes, furnish solutions of which the densities and coefficients of expansion are the means of those of the constituents. The *relative* strengths of corresponding solutions are indicated by the values of the coefficient μ . n = number of gram-molecules or half-molecules per litre—



Solutions correspond electrically when the means of their specific resistances and conductivities *most nearly* approach the resistances and conductivities of their mixtures in equal volumes. Electrical measurements were made by Kohlrausch's method, and are given in tables for each salt. These solutions contain



The resistance of a mixture of two solutions is almost always less than the arithmetic mean of the resistances of the separate solutions. For corresponding solutions, the difference is a minimum.

A similarly simple law does not hold for the conductivities of mixtures. Thus solutions of NaCl and NH_4Cl , and of KCl and $\frac{1}{2}\text{BaCl}_2$, correspond as regards conductivity in two very different relative states of concentration. The idea of correspondence is therefore based primarily on resistance.

The author answers the objection of Arrhenius (Abstr., 1887, 415), that correspondence is based on a purely arithmetical relation, and points out that this relation is more general, and not more arbitrary, than that on which Arrhenius founds his idea of “isohydric” solutions. Ch. B.

Compressibility of dilute Salt Solutions and of solid Sodium Chloride. By W. C. RÖNTGEN and J. SCHNEIDER (*Ann. Phys. Chem.* [2], **31**, 1000—1005).—Schumann (Abstr., 1887, 696) states that weak solutions of potassium and calcium chlorides at 15°, and of ammonium and strontium chlorides at 0°, are more compressible than pure water. In their previous work (*Ann. Phys. Chem.*

[2], 29, 165), the authors have not observed such an anomaly. They have therefore repeated Schumann's experiments as nearly as possible, but with entirely opposite results. No details are given.

The authors also state that they have found no perceptible difference between the compressibilities of air-free water and of water saturated with air at ordinary temperature and pressure. The difference, at any rate, is less than 0.2 per cent.

By methods already described, they have also found the relative apparent compressibility of solid sodium chloride = 0.049. This value is not very different from the number 0.044, which is obtained when the interpolation formula for the relative apparent compressibility of sodium chloride solution (*loc. cit.*) is extended beyond the limits of solubility of the chloride, and n put = ∞ . It may perhaps be possible in this way from the known compressibility of a solution to calculate, at least approximately, that of the dissolved solid. The above direct determination gives for the true compressibility 5.0×10^{-6} . By calculation from the interpolation formula, the number 4.8×10^{-6} , and from the formula for the relative molecular compressibility the number 4.7×10^{-6} , are obtained.

These numbers differ greatly from that obtained by Braun (Abstr., 1887, 436), namely, 1.4×10^{-6} . The authors therefore give details of their own experiments. They have further made determinations, using comparatively low pressures, in order to eliminate errors due to inclusion of air in crevices in the crystals. These led to the above number 0.049. Ch. B.

Water of Crystallisation of dissolved Cobalt Salts. By J. KALLIE (*Ann. Phys. Chem.* [2], 31, 1015—1028).—It is known that the dehydration by heat of cobalt chloride in solution is effected at a lower temperature when the solution is saturated with sodium chloride. The author has studied this reaction quantitatively by observing the accompanying changes in the absorption-spectrum in the neighbourhood of the D line. Let A be the absorption coefficient for a known solution of the hydrated salt of thickness d , E that of the same solution when dehydration is complete, and M the coefficient when at any temperature a fraction $1/x$ has been converted. In the latter case, the absorption will be equivalent to that produced by a thickness d/x of dehydrated solution, and a thickness $d - d/x$ of unchanged solution, whence—

$$M = A^{(1 - \frac{1}{x})}. \quad E^{\frac{1}{x}} \text{ and } \frac{1}{x} = \frac{\log M - \log A}{\log E - \log A}.$$

A beam of parallel rays from a petroleum lamp, or from the sun, was directed perpendicularly upon a glass trough with parallel sides containing the solutions under experiment (0.0746 gram of CoCl_2 per litre). The coefficients were measured by Glan's photometer (*Ann. Phys. Chem.* [2], 1, 351; 12, 481; 14, 177; and 15, 337). The conversion was assumed to be complete when rise of temperature caused no further change in the absorption. This occurred at 84° for a saturated salt solution, at 94° when the solution contained 1.12 grams NaCl to 5.22 grams cobalt solution. In any particular solution, the

absorption is constant for a given temperature. The trough was heated by means of an air-bath. Curves having the temperatures in degrees as abscissæ, and the percentages of dehydrated salt as ordinates, were then traced for each sodium chloride solution.

These curves show that in each case the dehydration is continuous; no intermediate hydrate is formed. The actual composition of the final salt, CoCl_2 or $\text{CoCl}_2 + \text{Aq}$, is unknown. The rate at which dehydration takes place is more rapid the higher the temperature. At low temperatures, the curves for different salt solutions are congruent; and as a rule, one curve can be converted into another by moving each point of it along the abscissa through a definite number of units. The course of the conversion is thus always the same, and is independent of the amount of cobalt in solution; the presence of sodium chloride simply transfers it to a lower range of temperature. In a pure cobalt chloride solution, the conversion is very slight below 100° .

Experiments were also made with sodium bromide and iodide. The greatest effect is produced by the chloride, the least by the iodide. With the bromide and iodide, the action is not very regular; probably because the *degree* of saturation is lowered as the temperature rises.

CH. B.

Condensation of Water Vapour by Solid Substances. By T. IHMORI (*Ann. Phys. Chem.* [2], **31**, 1006—1014).—A continuation of previous experiments (Warburg and Ihmori, *ibid.*, **27**, 481). The author has improved the construction of the balance there described, avoiding the use of sealing-wax, which is hygroscopic, and of brass, which becomes so by oxidation. Platinum is used instead.

Sealing-wax, shellac, and metallic surfaces varnished with shellac, are very hygroscopic. Bright metal surfaces take up very little water; but if oxidation occurs, the surface may become rather hygroscopic. Water taken up by such a surface is only partly given off in a dry vacuum.

Agate is also very hygroscopic: the absorption appears to vary with the colour. Rock crystal is very slightly hygroscopic, especially after cleaning with leather, or, still better, washing with hot water. After the latter treatment, the absorption becomes zero or negative.

Platinum condenses water very slightly; the condensation disappears entirely after rubbing with leather. Old platinum may require heating to redness, probably in order to destroy a film of grease.

In the author's opinion, a sensitive balance should have all metallic parts platinised; neither shellac varnish nor agate should be used in its construction; rock crystal might, perhaps, be substituted for the latter. Platinum or platinised brass is preferable to rock crystal for weights.

Experiments with glass are also described.

CH. B.

Rate of Oxidation of Carbon Compounds by Potassium Permanganate. By DREYFUS (*Compt. rend.*, **105**, 523—525).—When the oxidation of carbon compounds by potassium permanganate reaches

its limit, the quantities of oxygen absorbed by equal weights of different compounds are not identical, but are of the same order of magnitude. When, however, the action is restrained, and the rate of oxidation is measured, the results vary widely with different compounds.

The reagents employed consisted of a potassium permanganate solution equivalent to a solution of 0.1 gram of crystallised oxalic acid per litre, and a solution of indigocarmine, 10 c.c. of which was equal to 5 c.c. of the permanganate. A 1 per cent. solution of ethyl alcohol was used as a standard liquid, and all the other solutions were compared with it, the rate of oxidation of ethyl alcohol being taken as unity. 50 c.c. of the alcohol solution was placed in a cylinder, and an equal volume of the solution to be examined in another cylinder, 25 drops of sulphuric acid was added to each, and after two minutes 10 c.c. of potassium permanganate. The cylinders were allowed to remain in diffused light at about 15° , and 10 minutes after the permanganate had been added to the alcohol, the latter was run into 10 c.c. of the indigocarmine solution until the colour of the latter changed to yellow. Two minutes later, the other solution was treated in the same way. A simple calculation gives the quantity of oxygen absorbed by each substance under conditions which are strictly comparable, except that the weights of the substances are not identical. The second solution is diluted to a suitable extent, and after two or three comparative experiments, it is easy to calculate the amount of water to be added to the second substance, in order that the quantity of oxygen absorbed may be the same in both cylinders, and from this we get the weight p of the substance which will absorb as much oxygen in a given time as 1 gram of ethyl alcohol. If the two numbers 1 and $\frac{1}{p}$ are not actually proportional to the rates of oxidation of equal weights of the two substances, they are of the same order, and may be regarded as coefficients of the relative rates of oxidation of the various compounds.

A large number of substances were examined, and the rates of oxidation vary from 0.2 in the case of saccharose to 10,000 in the case of pyrogallol; next in order to pyrogallol comes catechol, quinol, and resorcinol, with 5000, 3333, and 2000 respectively, phenol 786.0, α -naphthol 769.00, and β -naphthol 666.0. Hydrocarbons, sugars, alcohols of the ethyl series, and acids of the acetic and benzoic series, have much lower rates, varying from 1.0 to 6.0. Ether and alcohol show identical velocities.

Determinations of the rate of oxidation may be used to determine the class to which a substance belongs, and also to detect impurities in such compounds as acetone. The constitution of compounds affects the rate of oxidation more than their composition. Other conditions being the same, a saturated compound is less active than a non-saturated compound. Substances of the same chemical function show comparable rates of oxidation. The aldehyde function is more active than the alcoholic, and the phenolic function shows a very much greater activity. The rates of oxidation of isomerides are not the same. In the case of the dihydroxybenzenes and the toluidines, the

ortho-derivative absorbs the most oxygen, and the meta-derivative the least, the para-derivative occupying an intermediate position.

C. H. B.

Laboratory Fittings. By J. GIBSON (*J. Soc. Chem. Ind.*, **6**, 205—211).—The following is a list of fittings and apparatus in use at the new chemical laboratories of the University of Edinburgh:—(1) System of ventilation and fume extraction, the draught being produced by a Blackman air propeller; the great power of the draught has rendered it possible to dispense with draught cupboards almost entirely; (2) draught arrangements on the working tables; (3) utilisation of the draught in connection with steam-baths; (4) arrangement for supplying the laboratories with water at a high and constant pressure; (5) gas, water, and steam supply to a stone table intended for combustion and similar operations; (5) convenient arrangement of draught, gas, and steam supply to a small draught cupboard; (7) new substitute for a sand-bath; (8) improved filtering apparatus; (9) apparatus for preserving gaseous hydrogen sulphide. D. B.

Inorganic Chemistry.

Compound of Iodine with Ammonia. By F. RASCHIG (*Annalen*, **241**, 253—255).—Iodine absorbs dry ammonia gas, forming a dark-blue liquid; Bineau (*Ann. Chim. Phys.* [3], **15**, 80) assigns to this substance the formula $3\text{NH}_3, 2\text{I}$, but according to Millon (*Annalen*, **62**, 54) iodine absorbs less than half the volume represented by this formula. The author finds that the volume of ammonia absorbed by the iodine varies with the temperature. At 20° , the amount of ammonia absorbed corresponds with Bineau's formula, but at 80° it corresponds with NH_3I , at 0° with $\text{I}(\text{NH}_3)_2$, and at -10° with $\text{I}_2(\text{NH}_3)_5$. The liquid is decomposed by water, yielding ammonium iodide and nitrogen iodide, but it dissolves completely in alcohol without undergoing any change. W. C. W.

Method for Decomposing Arsenical Sulphides. By H. WARREN (*Chem. News*, **56**, 193—194).—The cobalt speiss or arsenical alloy is digested in hydrochloric acid containing copper nitrate, and after a day or so, the insoluble portions are calcined at a low red heat with plentiful access of air; the calcined mass is then easily dissolved by hydrochloric acid and mixed with the other solution. The copper is separated by means of metallic iron, which also removes some bismuth and arsenic; and the iron and remaining arsenic are precipitated by adding milk of lime. The calcium salts are removed by treatment with sulphuric acid, and the solution containing nickel and cobalt is precipitated by means of sodium carbonate. The precipitate is then suspended in water and chlorine passed to saturation, when the nickel goes into solution, whilst the cobalt remains undissolved. The solu-

tion is boiled, and on adding caustic soda the nickel is obtained as hydroxide, which is ignited and reduced in the usual way.

D. A. L.

Zinc Titanates. By L. LEVY (*Compt. rend.*, **105**, 378—380).—When a mixture of 6 grams of titanic oxide, 2.5 grams of zinc oxide, and 5 to 10 grams of anhydrous zinc chloride is heated in a glass tube, the reaction is incomplete, and a violet product is obtained which contains an excess of titanic oxide. With excess of zinc chloride, the product is yellowish. If the mixture is heated in a Perrot's furnace in a crucible brasqued with charcoal and rutile, the zinc chloride volatilises, but if the heating takes place in a long porcelain tube closed at one end, a violet or green, crystalline mass is formed, which contains titanium, zinc, silicon, and potassium.

If a mixture of 7 grams of titanium oxide, 5 grams of zinc oxide, and a small quantity of zinc fluoride, or 7 grams of titanium oxide and 30 grams of zinc fluoride is heated under a thin layer of potassium fluoride in a graphite crucible in a Perrot's furnace for an hour and a half, washed with water, and then treated with concentrated sulphuric acid to remove zinc oxide and titanium fluoride, beautiful violet needles are obtained. With potassium chloride in place of the fluoride, the product is a greenish mass. With a mixture of potassium and sodium chlorides the violet needles are obtained mixed with yellowish needles of potassium titanate. The violet crystals are zinc trititanate, $\text{ZnO} \cdot 3\text{TiO}_2$, a small quantity of the zinc being displaced by iron. They are insoluble in water, alcohol, and ether, are not affected by hot dilute sulphuric, nitric, and hydrochloric acids, nor by boiling concentrated solutions of alkaline hydroxides, but are attacked with difficulty by boiling concentrated sulphuric acid, and are decomposed by fusion with potash. They are infusible before the blowpipe, but change to a greenish mass without loss of weight; sp. gr. at $15^\circ = 4.92$. The crystals are not attacked by hydrogen at a red heat, but partially volatilise in a mixture of chlorine and hydrogen chloride. When treated with acidified hydrogen peroxide, the latter acquires a characteristic yellow colour, but decomposition is never complete.

C. H. B.

Electrolytic Method of preparing Metallic Alloys, &c. By H. WARREN (*Chem. News*, **56**, 153—154).—The following method is recommended for the preparation of alloys such as phosphor-bronzes, silicides, &c. The metal and substance containing alloying material are placed in a deep, conical crucible, through the bottom of which passes a rod of graphite, extending about one inch within the crucible and protected on the outside by an iron tube. The metal is melted and the graphite put in connection with the negative pole, whilst the molten substance on the surface is connected with the positive pole of a battery of two large ferric chloride cells. In this manner silicon copper and silicon-eisen are easily prepared from potassium silicofluoride and the respective metal; the salt being taken in sufficient quantity to form a molten layer 2 inches deep. By some slight variation in the details, phosphor-bronzes can be produced; moreover, native cryolite can be decomposed in contact with metallic zinc, and on

subsequently volatilising the zinc, pure aluminium is obtained. Magnesium, barium, strontium, and calcium have not yielded satisfactory alloys as yet. D. A. L.

Process for obtaining the Rare Earths from the Ceriferous Hainstadt Clays. By J. R. STROHECKER (*Chem. News*, 56, 175—176).

—The author attributes the failure of other chemists to obtain cerium from these clays (compare Abstr., 1886, 678) to the fact that in the presence of more than 0.5 per cent. of iron, the cerium precipitated by oxalic acid and potassium sulphate is much contaminated with iron, the oxide prepared therefrom being so coloured by iron oxide as to be mistaken for that substance. He describes the processes by which he affirms that he has separated the various rare earths from these clays. A. J. G.

Reduction of Aluminium Oxide. By G. A. FAURIE (*Compt. rend.*, 105, 494).—Two parts of pure finely-powdered aluminium oxide is made into a paste with one part of petroleum or some other hydrocarbon, and then mixed with one part of sulphuric acid. When the mass is homogeneous with a pale yellow tint, and begins to give off sulphurous anhydride, it is wrapped in paper and thrown into a crucible heated to above 800° in order to decompose the hydrocarbon. The compact product thus obtained is powdered and mixed with its own weight of a finely-divided metal, the mixture being then heated to a white heat in a plumbago crucible. The regulus after being allowed to cool is found to contain grains of an aluminium alloy in the midst of a metallic powder.

This method of reduction is applicable to silica, calcium oxide, magnesium oxide, &c. C. H. B.

Halogen Compounds of Gold. By G. KRÜSS and F. W. SCHMIDT (*Ber.*, 20, 2634—2643).—Experiments made with a view to prepare aurous chloride and bromide by the action of chlorine and bromine respectively on gold, gave negative results. The gold is converted into auric compounds in both cases; it is difficult to complete the reaction. It is suggested that the numbers obtained by Thomsen, pointing to the formula Au_2Cl_4 , were obtained from a product from which the adhering chlorine had not been removed. When gold is warmed in bromine vapour, a black compound is formed which decomposes into its constituents when heated at 100°, even when kept in bromine vapour. The product contains a large amount of unattacked gold together with auric bromide. The compound Au_2Br_4 is not formed.

The authors conclude that Thomsen's auro-auric chloride and bromide (this Journal, 1877, ii, 485) do not exist. N. H. M.

Gold Sulphides. By L. HOFFMANN and G. KRÜSS (*Ber.*, 20, 2704—2710).—Oberkampf believed that he obtained an auro-auric sulphide, Au_2S_2 , by heating a solution of auric chloride with hydrogen sulphide, but the product, according to Levöl and Fellenberg, had a composition varying between that of Au_2S_2 and Au_2S_3 , whilst Schrötter and Priwoznik state that an auro-auric sulphide of constant composi-

tion cannot be obtained. These results are probably to be attributed to an incomplete removal, by mere washing on a filter, of sulphur precipitated simultaneously, since the authors find that to remove free sulphur from the precipitate it is necessary to wash the sulphide by decantation with absolute alcohol, anhydrous ether, and carbon bisulphide successively (compare Abstr., 1887, 1019).

When a neutral solution of auric chloride is treated with hydrogen sulphide in the cold until all colour has disappeared from the solution, and the precipitate, after repeated washing with water, is washed by decantation as above, auro-auric sulphide, Au_2S_2 , of constant composition is obtained, and the reaction is represented quantitatively by Levöl's equation, $8\text{AuCl}_3 + 9\text{H}_2\text{S} + 4\text{H}_2\text{O} = 4\text{Au}_2\text{S}_2 + 24\text{HCl} + \text{H}_2\text{SO}_4$. Auro-auric sulphide is a black powder in the dry state, and when moist is also black by reflected light, but in the finely-divided state it transmits light of a reddish-brown colour. On porcelain, it gives a black streak. When heated in a tube, sulphur begins to volatilise at 140° , as sulphurous anhydride, and is completely expelled at $250\text{--}270^\circ$ without the intermediate formation of aurous sulphide. With the exception of aqua regia, auro-auric sulphide is insoluble in all acids. Bromine water gradually converts it, especially on warming, into auric bromide and sulphuric acid. Alkaline monosulphides dissolve it slowly in the cold, but readily on heating, yielding brown solutions which become greenish-yellow when the heating is continued; alkaline polysulphides dissolve it in the cold, and the solutions on heating become brown and eventually yellow; yellow sulphide of ammonium, however, dissolves the compound less readily than the sulphides of the alkalis. Concentrated aqueous potash does not attack it in the cold, but on heating converts it into gold, potassium gold sulphide, and potassium gold oxide. Potassium cyanide dissolves it readily. When heated in a current of oxygen, the sulphide ignites, and is converted into gold and sulphurous anhydride, whilst hydrogen sulphide is formed when the heating occurs in a current of hydrogen.

By fusing gold with potassium pentasulphide, Berzelius states that he obtained a sulphide which he believed to have the composition Au_2S_3 , although no analyses were made. The authors have endeavoured to prepare a gold sulphide of this composition in four ways:—(1) By Berzelius' method; (2) by Oberkampff's and by Yorke's method (this Journal, 1848, 236), which consists in precipitating a saturated solution of auro-auric sulphide in sodium bisulphide with an acid; (3) by precipitating a saturated solution of auro-auric sulphide in sodium monosulphide with hydrochloric acid; and (4) saturating a solution of sodium gold oxide with hydrogen sulphide and heating the normal sodium thioaurate with an acid; the precipitates in every case were washed by decantation with alcohol, ether, and carbon bisulphide. The precipitated sulphide obtained by the first two methods, however, contained more sulphur than required for the formula Au_2S_3 , and had not a constant composition; whilst that prepared by the last two methods had a composition intermediate between that of Au_2S_2 and Au_2S_3 . The authors therefore conclude that auric sulphide, Au_2S_3 , does not exist, and show that the properties of the so-called com-

pound are those of a mixture of auro-auroic sulphide and sulphur, the latter being left as an insoluble, white powder on digestion with potassium cyanide.

W. P. W.

Mineralogical Chemistry.

Cliftonite, a Cubic Form of Graphitic Carbon. By L. FLETCHER (*Min. Mag.*, 7, 121—130).—A meteoritic iron found on 5th January, 1884, in the district of Youndegin, Western Australia, contains a remarkable form of carbon resembling graphite but crystallising in the cubic form. Four fragments of the meteorite were found, weighing $25\frac{3}{4}$, 24, 17, and 6 lbs. respectively. In addition there was about 17 lbs. of what appeared to be an outer shell, doubtless due to the weathering of the original mass. The meteorite is extremely hard, and contains numerous inclusions of schreibersite. It has a sp. gr. of 7·85. No distinct figures were obtained on etching. Analysis gave—

Fe.	Ni.	Co.	Cu.	Mg.	P.	S.	Insol. cubes.	Total.
92·67	6·46	0·55	trace	0·42	0·24	nil	0·04	100·38

The insoluble residue consists of about a hundred small cubes of an opaque greyish-black mineral with metallic lustre. The hardness is 2·5, the sp. gr. 2·12, and the streak black and shining. It is not attacked by acids, and but slowly by fused nitre. It burns away very slowly in air, leaving a minute residue. Chemical tests show that the residue resembles graphite, but it is harder and occurs in definite cubic crystals. The author is of opinion that it is an allotropic modification of carbon distinct from diamond and graphite, and names it *cliftonite* after Professor R. B. Clifton, of Oxford. B. H. B.

Natural Gas of Pennsylvania. By K. SORGE (*Jahrb. f. Min.*, 1887, ii, Ref., 318—320; from *Stahl und Eisen*, 7, 93—108).—Since 1821, natural gas has been used in Pennsylvania in a limited and irregular way for illuminating and heating purposes. Since 1883, however, it has attained an extraordinarily rapid development for industrial purposes. At the present time, 15 towns are supplied with natural gas.

The chemical composition of the gas varies in the different wells, and even in the same well after a short lapse of time. In all cases, marsh-gas is the principal constituent. The mean volumetric composition of the gas is as follows:—

CH ₄ .	H.	O.	N.	C ₂ H ₆ .	C ₂ H ₄ .	CO ₂ .	CO.	Total.
67	22	0·8	3	5	1	0·6	0·6	100·0

The composition is said to vary within the following limits:—

CH ₄ .	H.	N.	C ₂ H ₆ .	C ₃ H ₈ .	CO ₂ .	CO.
60—80	5—20	1—12	1—8	0—2	0·3—2	trace

Experiments made by Ford show that gas from the same well may vary considerably. In the gas-pipes of the Edgar Thomson steel-works at Pittsburgh, on different days, the gas contained per cent. :—

Nitrogen.	Carbonic anhydride.	Oxygen.
0 to 23	0 to 2	0·4 to 4

The natural gas of Pennsylvania is strikingly similar in composition to the illuminating gas obtained from Westphalian gas-coal.

B. H. B.

Servian Coal. By S. M. LOSANITSCH (*Ber.*, 20, 2716—2718).—Large coal seams occur in Servia in strata varying in age from that of the carboniferous to that of the tertiary formations, and in the paper, analyses are given of graphite, of 33 specimens of coal, and of 4 specimens of shale yielding paraffin, obtained from different localities. Corrections are applied for the amount of hygroscopic water and of ash in the estimation of the percentage of volatile matter and coke obtained from each sample of coal. The table (p. 32) gives the percentage composition of the samples of coal from each formation yielding the greatest and least number of calories respectively.

On dry distillation, the paraffin shale from Subotinci gave the following results:—Tar, 34·00; water, 8·00; ash, 29·25; carbon (in the ash), 17·28; gas, 11·47. A poorer specimen gave 10 per cent. of tar, and the shale from Mijonica, from Orašac, and from Bovan, gave 7 to 18 per cent., 31·5 per cent., and 30 per cent. of tar respectively.

W. P. W.

Ullmannite from Lölling and from Sarrabus. By C. KLEIN and P. JANNASCH (*Jahrb. f. Min.*, 1887, ii, Mem., 169—173).—The ullmannite, NiSbS, discovered at Sarrabus in Sardinia in 1883, crystallises in the regular system in hemihedral crystals with parallel faces. A comparison of this mineral with the hemihedral crystals with inclined faces, having the same empirical constitution, had previously not been instituted. The authors having secured some of the extremely rare material from Lölling, have now been enabled to make the comparison.

The percentage compositions of the ullmannites analysed were as follows :—

	S.	Sb.	As.	Ni.	Co.	Fe.	Insoluble.	Total.	Sp. gr.
I.	14·69	55·71	1·38	28·13	0·25	0·09	0·27	100·52	6·625
II.	14·64	55·73	0·75	28·17	trace	0·17	0·11	99·57	6·733

I. Ullmannite from Lölling; II. from Sarrabus.

It is thus evident that the two specimens have the same chemical composition and specific gravity. Crystallographical investigations, however, prove that the Lölling crystals are hemihedral with inclined faces, whilst the Sarrabus crystals are hemihedral with parallel faces. The authors are unable to prove that these differences are only apparent, and that the crystals are tetartohedral.

B. H. B.

Bismuthite from the Transvaal. By H. LOUIS (*Min. Mag.*, 7, 139—140).—Bismuthite occurs plentifully, though finely disseminated,

Description and source.	Locality.	C.	H.	O (& N).	H ₂ O.	Ash.	Volatile matter.	Coke.	Calories.
Graphite	Stol	92.59	—	—	0.46	6.95	—	—	—
Coal (3) from carboniferous formations	Mustapić-Mišljenovac	82.61	3.99	6.48	0.95	5.96	17.17	75.92	7725
	Kladurovo	74.34	3.69	4.80	1.12	16.77	—	—	7007
Coal (6) from Jura formations	Prijita	86.42	3.81	4.06	1.18	4.53	10.94	83.35	8089
	Milanovac donji	64.54	3.40	11.04	1.80	19.29	17.23	61.77	5845
Coal (12) from chalk formations	Mrtvica	63.42	4.60	18.55	6.10	7.33	37.12	49.45	5771
	Jelovac	51.75	3.47	21.39	13.08	10.31	37.02	39.59	4257
Coal (12) from tertiary formations.	Miliva	59.44	4.14	24.73	10.33	1.86	40.70	47.61	5158
	Kostolac	43.45	3.10	19.19	24.93	8.71	39.61	27.65	3497
	Subotinci	47.23	6.80	12.13	3.90	29.94	49.36	16.80	5541
Paraffin shale	Mijonica	17.09	2.32	12.60	1.70	66.23	29.61	2.48	—

in the auriferous quartz veins in the Lydenburg district of the Transvaal. It is amorphous, pulverulent, opaque, and of a yellow colour. Its hardness is about 3, and its sp. gr. 6·86. Analysis gave the following results:—

Quartz.	Bi_2O_3 .	CO_2 .	H_2O .	Fe_2O_3 .	Total.
0·9	79·6	7·2	2·7	9·6	100·0

This corresponds with the formula $\text{Bi}_2\text{H}_2\text{CO}_6$. A similar paragenesis of bismuthite with auriferous quartz has been recorded from South Carolina. B. H. B.

Barytes in the Carpathians. By F. v. HAUER (*Jahrb. f. Min.*, 1887, ii, Ref., 284; from *Verh. d. geol. Reichsanst.*, 18, 387).—About three-quarters of a mile to the north-west of Losoncz, an extensive deposit of barytes has been found in association with the melaphyre which bursts through the new red sandstone at that locality. The mineral exhibits a coarsely crystalline texture, and has a sp. gr. of 4·47. Fully developed crystals are not found. B. H. B.

Identity of Dreeelite and Barytes. By A. LACROIX (*Jahrb. f. Min.*, 1887, ii, Ref., 266; from *Bull. Soc. Franc. Min.*, 8, 435—437).—The mineral termed dreeelite by Dufrénoy is shown by the angles of the cleavage planes and by the optical characters to be identical with barytes. On account of deficiency of material, an analysis was impossible. Probably, however, the percentage of calcium sulphate given by Dufrénoy was due to impurities. B. H. B.

Titanite. By K. BUSZ (*Jahrb. f. Min.*, 5, Beilage, 330—380).—This elaborate monograph is divided into two parts, one giving the results of a chemical and optical examination of a large number of specimens of titanite, the other giving the results of the crystallographical examination. The research was undertaken primarily to determine whether there is any relation between the chemical composition of titanite and its optical constants. The specimens examined were from the following 10 localities:—Schwarzenstein in the Zillerthal, Eisbruckalp, Val Maggia, St. Gothard, Wildkreuzjoch in Tyrol, Laacher See, Arendal in Norway, Renfrew and Grenville in Canada, and Monroe in Michigan. As a rule, the author finds that in titanites containing iron, the angle of the optic axes is larger than that of titanites containing no iron. Exceptions to this rule are, the titanite from Monroe, which with a very high percentage of iron has a comparatively small axial angle, and the titanite from the Zillerthal, which with 1·07 per cent. of ferric oxide has the smallest axial angle of all the titanites examined. It is, however, evident that the magnitude of the axial angle of titanites rich in iron is not in proportion to the percentage of iron.

In his crystallographic investigation, the author observed 75 planes occurring on titanite crystals. Of this number, 22 have not hitherto been observed. B. H. B.

Palæopicroite of Amelose and the Products of its Alteration. By R. BRAUNS (*Jahrb. f. Min.*, 5, Beilage, 275—329).—Since 1831, when Breithaupt first showed that the well-known crystals found at Snarum, Norway, were pseudomorphs of serpentine after olivine, the alteration of olivine and the new minerals formed thereby have frequently been the objects of careful investigation. In no place, however, is the immediate connection of olivine with the products of its alteration so apparent as at Amelose, near Biendenkopf, in Hesse, where within an area of a hundred square yards is found not only the olivine rock in place, but also all the recent minerals formed from it. The latter include serpentine, chrysotile, metaxite, picrolite, a new magnesium iron silicate, calcite, and quartzite interesting on account of the occurrence of the extremely rare planes $\frac{3}{4}R\frac{3}{2}$, $\frac{5}{6}R\frac{5}{4}$. The matrix of these minerals differs from that of most serpentines in that it is of Devonian age, and not interstratified in crystalline schists. It is, in fact, an olivine-diabase (palæopicroite).

The new mineral is named by the author *webskyite*, after the late Professor Websky of Berlin. It is amorphous, and has a pitch-black colour with a brownish-green streak. In thin fragments, the colour is bright green. The hardness is 3, and the sp. gr. only 1.771. Its constituents are qualitatively the same as those of serpentine. Its quantitative composition, however, is different, since it contains 31 per cent. of water, 21 per cent. of which is lost at 100°. Analysis shows that the mineral has the formula $H_6R_4Si_3O_{13} + 6H_2O$, in which R represents Mg and Fe. The new mineral is probably of more frequent occurrence than might be imagined; the author having discovered it on specimens of diopside and of serpentine in the Berlin and Marburg museums.

B. H. B.

A Variety of Granulite, the Matrix of two New Minerals. By H. SAUER (*Jahrb. f. Min.*, 1887, ii, Ref., 295; from *Zeit. deutsch. geol. Ges.*, 38, 704—706).—In a new quarry by the railway station of Waldheim in Saxony, the following two new minerals were found in the granulite:—*Prismatine*, crystallising in rhombic prisms without terminal planes, grouped radially. It resembles andalusite or sillimanite. Its composition is given under I. It easily alters to a finely fibrous substance, termed *cryptotile* (Analysis II):—

	SiO ₂ .	Al ₂ O ₃ .	FeO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
I.	30.89	43.06	6.28	15.08	2.04	0.79	1.36	99.50
II.	48.43	41.63	—	2.13	—	—	7.70	99.89

B. H. B.

Rocks from the Congo. By C. KLEMENT (*Jahrb. f. Min.*, 1887, ii, Ref., 300—301; from *Tschermak Min. Mitth.*, 8, 1—27).—The author gives analyses of two specimens of laterite from the Congo. They are composed of a conglomerate of quartz grains cemented by a brown to yellowish-red material. The red rock (I) is more porous than the brown (II), and seems to be a product of the decomposition of the latter. These laterites are said to be a detritus of the crystalline schists in the interior of the continent. For the analyses, the material was freed from the coarsest quartz grains.

	SiO ₂ .	P ₂ O ₅ .	SO ₃ .	Cl.	Fe ₂ O ₃ .	FeO.	Al ₂ O ₃ .	CaO.	MgO.
I.	52.91	0.51	0.29	0.08	36.26	0.29	4.13	0.19	0.07
II.	63.08	1.22	0.27	0.13	27.65	0.52	2.30	0.57	0.41
			Na ₂ O.	K ₂ O.	H ₂ O.	Total.			
			I. 0.08	0.04	6.16	101.01			
			II. 0.19	0.06	4.71	101.11			

B. H. B.

The Water Supply of Oderzo. By M. SPICA and G. HALAGIAN (*Gazzetta*, 17, 317—323).—The water supply of the municipality of Oderzo is taken from three mountain springs, Monticano, Lia, and Navisego, which pass through a clay soil. The analyses tabulated below show that these waters are of the highest order of purity. The colour viewed through a tube was a pale-yellow. With an alcoholic solution of tannin (Hager's test), they remained perfectly clear for several days. With phenolphthalein, they showed no reaction, but with litmus they appeared slightly alkaline.

Results of Analyses expressed in grams per litre.

	Monticano.	Lia.	Navisego.
Total residue	0.31	0.287	0.289
Chlorine	0.00797	0.00206	0.00197
Sulphuric anhydride.....	0.02782	0.04703	0.04446
Silica	0.001	0.00425	0.0028
Ferric oxide and alumina.....	0.0015	0.00125	0.003
Lime	0.08888	0.09188	0.09632
Magnesia	0.06036	0.03081	0.03099
Nitric acid		very slight traces	
Organic matter	0.02136	0.01583	0.01939
Oxygen required for organic matter.	0.00108	0.0008	0.00098
Total carbonic acid	0.2064	0.168	0.175
Free carbonic acid.....	0.1004	0.0841	0.0853
Total hardness } French {	24°·0	23°·5	27°·0
Permanent „ } scale {	12°·0	12°·4	13°·0

V. H. V.

Organic Chemistry.

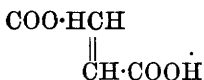
Arrangement in Space of the Atoms in the Molecules of Carbon-compounds. By J. WISLICENUS (*Chem. Centr.*, 1887, 1005—1009).—Van't Hoff and Le Bel were the first to explain the optical difference of certain carbon-compounds by a difference in the relative arrangement of the atoms in space within the molecule; since their work, however, no serious attempt has been made to apply their theory to explain the isomerism of certain compounds, whose composition, according to present views, is identical.

Such peculiar cases as those established by the researches of Fittig on the isomerism of maleic and fumaric acids, however, and the discovery of a third and fourth monobromocinnamic acid, have been classified under the generic term of alloisomerism. Chemists hitherto seem to have contented themselves with a name.

Adopting the hypothesis of van't Hoff and Le Bel that the atoms occupy the solid angles of a tetrahedron, being arranged around a central carbon-atom it is evident that two carbon-atoms, associated together in the paraffinoid form of combination, would revolve around one common axis, passing through the point of union of the atoms and the direction of attraction of two associated atoms, such as those of hydrogen. When two carbon-atoms are combined together, as in the olefines, they can only revolve round an axis which is the straight line connecting the two common carbon-atoms.

Supposing all four of the affinities of the saturating atoms are unequal, then six isomerides are possible, in the case of two pairs three isomerides, and three also if two affinities are equal and two unequal. For maleic acid, van't Hoff has proposed the formula $\text{CH}\cdot\text{COOH}$

$\begin{array}{c} \parallel \\ \text{CH}\cdot\text{COOH} \end{array}$, so that for fumaric acid the formula will be



In order to explain the conversion of maleic into fumaric acid through the intervention of halogen-derivatives of succinic acid, it is supposed that the atoms combined with neighbouring carbon-atoms mutually react on one another according to their chemical affinity. Hence, it follows that two carbon-atoms combined together by one affinity, and being in a position by revolution around their axis to give way to this attraction, will so arrange themselves that the associated radicles interchange positions in the system. Such a relative arrangement will be stable in the cold, but at a higher temperature, as the interoscillation of the elements will be more frequent, there is a loosening of the affinities, and a different configuration ensues. When an unsaturated compound passes into one that is saturated, it is indifferent to which of the two carbon-atoms each particular radicle attaches itself; the compounds formed are identical. But if an atom is combined with two different radicles, then by addition an asymmetrical carbon-atom results according as the added atoms attach themselves to one or other position of affinity. This explains the formation of optically inactive compounds under these conditions, since both modifications are produced in equal quantities.

As regards the nomenclature of these different geometrically isomeric configurations, it is proposed to call the arrangement

$\begin{array}{c} aCb \\ \parallel \\ bCa \end{array}$ the centrally or axially symmetrical, and the arrangement $\begin{array}{c} aCb \\ \parallel \\ aCb \end{array}$

the plane symmetrical.

The following examples are given in illustration of the above

views:—Tolane dichloride exists in two modifications; according to the author's hypothesis, the modification of higher melting point, obtained by the direct chlorination of tolane, is the plane symmetrical $\text{Ph}\cdot\text{C}\cdot\text{Cl}$

$\begin{array}{c} \parallel \\ \text{Ph}\cdot\text{C}\cdot\text{Cl} \end{array}$, whilst the other is the axially symmetrical $\begin{array}{c} \parallel \\ \text{Cl}\cdot\text{C}\cdot\text{Ph} \end{array}$. As

fumaric acid is principally formed by heating malic acid, in which, doubtless, the carboxyl-group has more inclination towards the hydrogen-atom than to the hydroxyl- or other carboxyl-group, its constitution may be represented by a configuration $\begin{array}{c} \text{COOH}\cdot\text{CH}\cdot\text{OH} \\ | \\ \text{HH}\cdot\text{C}\cdot\text{COOH} \end{array}$,

from which by the abstraction of a molecule of water the formula $\text{COOH}\cdot\text{CH}$

$\begin{array}{c} \parallel \\ \text{HC}\cdot\text{COOH} \end{array}$ results. The conversion of ethyl maleate into ethyl

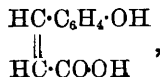
fumarate by iodine is explained by the intermediate formation of diiodosuccinnic acid, an interchange of position of the iodine- and hydrogen-atoms; the removal of a molecule of hydrogen iodide gives ethyl iodofumarate, which in its turn is reduced by the hydrogen iodide to ethyl fumarate.

The reverse process of conversion of fumaric into maleic acid through the intervention of dibromosuccinic acid can be explained in like manner. The isomerism of crotonic and isocrotonic acid is also of a similar order, the constitution of the one being expressible by a

formula $\begin{array}{c} \text{H}\cdot\text{C}\cdot\text{Me} \\ \parallel \\ \text{H}\cdot\text{C}\cdot\text{COOH} \end{array}$, of the other as $\begin{array}{c} \text{Me}\cdot\text{C}\cdot\text{H} \\ \parallel \\ \text{H}\cdot\text{C}\cdot\text{COOH} \end{array}$. Cinnamic acid

should also exist in two geometrically isomeric forms, of which, as yet, only one has been obtained.

β -Coumaric acid has the plane symmetrical arrangement



as it is easily converted into its lactone, coumarin; in its isomeride, the atoms are arranged in the axially symmetrical configuration; this, by fuming hydrobromic acid, is converted into coumarin, by temporary addition of a molecule of the acid, and by an inclination towards formation of the lactone.

By this theory, the removal of the elements of a halogen acid and simultaneously of carbonic anhydride from the sodium salt of a β -halogen substituted acid is explained, as also the formation of anhydrides and lactones when two carboxyl- or a hydroxyl- and carboxyl-group are in the γ -position.

The author is engaged on experimental evidence in favour of this theory. V. H. V.

Nitrosates, Nitrosites, and their Derivatives. By O. WALLACH (*Annalen*, 241, 288—315).—The crystalline compound which Guthrie

(*Annalen*, **116**, 248; **119**, 84) obtained by the direct union of amylene with nitrogen peroxide, is most conveniently prepared by passing the nitrous fumes evolved by the action of strong nitric acid on arsenious oxide into a well-cooled mixture of amylene (1 vol.) and glacial acetic acid (2 vols.). The operation is interrupted when the colour of the liquid changes from blue to green. The crystals are washed with acetic acid, afterwards with water. As commercial amylene is a mixture, the product is not homogeneous. On recrystallisation from chloroform or benzene, two substances having the composition $C_5H_{10}N_2O_4$ are deposited, namely, cubes melting at 96–97°, and needles melting at 89°. This compound is not a dinitrite but a nitroso-nitrate or *nitrosate*. On boiling with alcohol and aniline, it yields aniline nitrate and *amylene nitrolaniline*, $NHPh \cdot C_5H_9 : NOH$. The base melts at 140–141°. It dissolves freely in ether, chloroform, warm alcohol, and in dilute acids, and crystallises well. The *hydrochloride*, $C_{11}H_{16}N_2O \cdot HCl$, is deposited from a hot aqueous solution in anhydrous crystals. It is best prepared by passing hydrogen chloride into an ethereal solution of the base, when the hydrochloride is precipitated in the form of a crystalline powder. The *nitroso-compound*, $NO \cdot NPh \cdot C_5H_9 : NOH$, is deposited as a crystalline powder when a solution of sodium nitrite is poured into an acid solution of the base. It melts at 127–128°, and is soluble in alcohol and in alkalis. The nitroso-compound is reprecipitated on adding an acid to the alkaline solution. The hydrochloride is decomposed by boiling with water, or better with hydrochloric acid, yielding hydroxylamine and a ketone base, $NHPh \cdot C_5H_9 : O$. The new base melts at 61°, and is soluble in alcohol, ether, and in hot water.

Amylenenitrolparatoluidine, $C_{12}H_{18}N_2O$, and its hydrochloride and nitrate form well-developed crystals. The base melts at 111–112°, and the nitroso-derivative at 147–148°. The hydrochloride is decomposed on boiling it with hydrochloric acid, yielding hydroxylamine and the base $C_{12}H_{18}N_2O$ melting at 98°.

Amylenenitrolorthotoluidine melts at 115°. The nitroso-derivative melts with decomposition at 149–150°. The hydrochloride is more soluble in water than the corresponding para-salt.

Amylenenitrolorthoanisidine melts at 138–139°. The hydrochloride is deposited from its aqueous solution in prisms. Amylene nitrosate and piperidine act on each other very energetically, forming a crystalline base, $C_{10}H_{20}N_2O$. It melts at 95–96°, and is insoluble in water and in alkalis. The salts dissolve freely in water. The hydrochloride is an oily liquid, but the platinochloride $(C_{10}H_{20}N_2O)_2 \cdot H_2PtCl_6$ forms beautiful prisms. *Amylenenitroldiethylamine* crystallises in plates and melts at 71–72°. *Amylenenitrolallylamine* is soluble in water. The hydrochloride, $C_8H_{16}N_2O \cdot HCl$, is crystalline. This base is isomeric with nitrosoconiine.

Amylene nitrosate acts on sodium ethoxide, forming a crystalline compound which melts at 100°, and also on ethyl acetoacetate, yielding a crystalline compound of the composition



Guthrie (*loc. cit.*) observed that amyl nitrosate acts on potassium

cyanide, but the author finds that a crystalline compound and potassium nitrate, not a liquid and a *nitrite*, are formed in the reaction.

A blue crystalline compound is formed by passing nitrous fumes into bromanylene dissolved in acetic acid, and pouring the crude product into water. This compound acts on piperidine at the ordinary temperature, yielding a colourless, crystalline substance which exhibits neither acid nor basic properties. It is soluble in alcohol, is rich in bromine, and has an odour resembling that of camphor.

W. C. W.

Synthetical Experiments in the Sugar-group. By E. FISCHER and J. TAFEL (*Ber.*, 20, 2566—2575).—It was previously shown (*Abstr.*, 1887, 651) that acraldehyde bromide is converted by baryta into what is probably a glucose. With phenylhydrazine, the product of the reaction yields α - and β -phenylacrosazones, melting at 205° and 148° respectively.

When isoglucosamine oxalate (Fischer, *Abstr.*, 1886, 934) is dissolved in ice-water (10 parts) and treated with sodium nitrite, an evolution of nitrogen takes place; after three hours, the temperature is allowed to rise to 20°. The product is exactly neutralised with aqueous soda, evaporated in a vacuum, and the residue extracted with absolute alcohol. On evaporating the solution, levulose is obtained as a yellowish syrup; the spec. rotatory power at 80° = 25°. It produces strong fermentation with yeast in 10 minutes, gives a precipitate of phenylglucosazone with phenylhydrazine, and yields Kiliani's levulose hydrocyanide when treated with hydrocyanic acid. The constitution of isoglucosamine is probably $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot[\text{CH}(\text{OH})]_3\cdot\text{CH}_2\cdot\text{OH}$. Ledderhose's isomeric glucosamine has possibly the constitution $\text{CHO}\cdot\text{CH}(\text{NH}_2)\cdot[\text{CH}(\text{OH})]_3\cdot\text{CH}_2\cdot\text{OH}$.

α -Phenylacrosazone is obtained in the following manner: A solution of 75 grams of pure, crystallised barium hydroxide in 1.25 litre of water is cooled with ice-water; 50 grams of freshly-distilled acraldehyde bromide is then added by drops, the baryta solution being kept violently shaken. Eight preparations are united, made slightly acid with sulphuric acid, and treated with a strong solution of sodium sulphate until the barium is completely precipitated. After 12 hours, it is filtered, neutralised with aqueous soda, and evaporated in a vacuum to 1½ litre. When cold, a solution of phenylhydrazine hydrochloride (50 grams) and sodium acetate (50 grams) in 100 c.c. of water is added, and the whole left for 12 hours; it is then filtered and warmed on a water-bath with 150 grams more of phenylhydrazine hydrochloride and 150 grams of sodium acetate. In the course of four hours, a half crystalline and half resinous precipitate separates; this is washed with water and extracted with ether, when the greater part of the resin and the β -phenylacrosazone dissolves, leaving the α -phenylacrosazone. After filtration, the α -compound is repeatedly extracted with boiling alcohol, and treated with hot water, after which it is almost pure. The yield from 400 grams of bromide is 18 grams. It melts at 205° (uncorr.), and is very sparingly soluble. On adding water to the hot alcoholic solution, it separates in long, slender needles.

α -Acrosamine, $\text{C}_6\text{H}_{13}\text{NO}_5$, is prepared similarly to isoglucosamine

(*loc. cit.*) by reducing the acrosazone with zinc-dust and acetic acid, and is purified by means of the oxalate. It shows all the reactions of the glucosamines. When the oxalate is dissolved in ice-water and treated with sodium nitrite, α -acrose, $C_6H_{12}O_6$, is formed; this is obtained as a light-brown syrup, having a sweet taste. It reduces Fehling's solution.

β -Phenylacrosazone, $C_{18}H_{22}N_4O_4$, is obtained by evaporating its ethereal extract (obtained in the purification of the α -compound), dissolving in alcohol, and precipitating with water. The dried product is exhausted with cold benzene several times. The yellow crystalline residue is boiled with acetone (2 parts), filtered, and precipitated with ether and light petroleum. It crystallises in slender, yellow needles melting at 148° , dissolves in alcohol and acetone much more readily than the α -compound, but is almost insoluble in ether when pure. The yield is small.

The resemblance of α -phenylacrosazone to phenylglucosazone makes it probable that α -acrose has the constitution expressed by the formula $OH \cdot CH_2 \cdot [CH(OH)]_4 \cdot CHO$; the constitution of β -acrose would then be $OH \cdot CH_2 \cdot CH(OH) \cdot CH(OH) \cdot C(OH)(CH_2OH) \cdot CHO$ or



The lower melting point and more ready solubility of the β -osazone point to its being a derivative of a sugar with an abnormal carbon-chain.

Isodulcitolphenylhydrazine, $C_6H_{12}O_4 \cdot N_2HPh$, crystallises from alcohol in colourless plates melting at 159° . It is insoluble in ether, readily soluble in water and in alcohol. The aqueous solution is dextro-rotatory.

Lactosephenylhydrazine, $C_{16}H_{26}O_{10}N_2$, is prepared by adding phenylhydrazine (1 part) to a solution of milk-sugar (2 parts), in hot water (2 parts). After two days, twice the volume of absolute alcohol is added, and the whole treated with much ether. The syrupy precipitate after being repeatedly dissolved in alcohol and precipitated with ether, is obtained as a solid mass. It is filtered, quickly washed with ether, and dried in a vacuum over sulphuric acid. It dissolves readily in water and in alcohol, and is insoluble in ether. It is lævorotatory.

N. H. M.

Isonitrosogalactose. By P. RISCHBIETH (*Ber.*, 20, 2673—2674).—When galactose (1 gram) and hydroxylamine hydrochloride (0.4 gram) are dissolved in a small quantity of water, treated with sodium carbonate (0.65 gram), and allowed to remain for 24 hours, *isonitrosogalactose*, $C_6H_{12}O_5 \cdot NOH$, is obtained as a colourless, crystalline substance which melts at 175 — 176° , and is readily soluble in hot water, soluble in hot dilute alcohol, and practically insoluble in ether and absolute alcohol. Under similar conditions, no separation could be obtained from dextrose, levulose, or arabinose.

W. P. W.

The Carbohydrate Character of Formose. By C. WEHMER (*Ber.*, 20, 2614—2618).—Plants which readily produce starch from dextrose, cane-sugar, mannitol, and glycerol, do not produce starch in any determinable amount from formose.

When 28 grams of formose syrup is boiled with 100 c.c. of water and 5 grams of hydrochloric acid (sp. gr. 1.2) for 11 hours, a separation of humic substance (3.5 grams) takes place. The filtrate shows the iodoform reaction distinctly and reduces Fehling's solution. No levulinic acid is formed. 13 per cent. phosphoric acid produced the same decomposition, also without formation of levulinic acid.

The author concludes that formose is not a carbohydrate.

N. H. M.

Saccharification in Vegetable Tissues. By BONDONNEAU and FORET (*Compt. rend.*, **105**, 617—618).—The amylaceous plant is heated at 90—100° with acid of 1 to 2 per cent., and the starch is gradually and completely converted into dextrin, glucose, saccharose, &c., and the soluble products thus formed diffuse through the cell-walls into the surrounding liquid. When the proportion of sugar in the liquid ceases to increase, the process is finished. This method is readily applied on a large scale. The exhausted pulp is free from starch, but constitutes a valuable nitrogenous food-stuff for cattle. The pulp from maize has the composition,—Water, 79.15; ash, 1.22; nitrogenous matter, 8.38 (containing nitrogen, 1.31); oil, 5.48; cellulose and loss, 5.77 = 100. It will be observed that water has been substituted for the starch.

C. H. B.

Amines of the Paraffin and Benzene Series. By MALBOT (*Compt. rend.*, **105**, 574—576).—In the reactions described, unless otherwise stated, the substances were mixed in equal molecular proportions.

Ethylamine and aqueous ammonia at 100° yield triethylamine, but at 150° tetraethylammonium chloride is obtained in considerable quantity. Propyl iodide under the same conditions yields tripropylamine at 100°, and tetrapropylammonium iodide at 150°. Although pure tripropylamine combines but slowly with propyl iodide in the cold, combination becomes complete at 150°. Tripropylamine has no action on propyl chloride in the cold, and the reaction takes place slowly at 150°, but becomes very rapid at 190°, the products being tripropylamine and dipropylamine hydrochlorides and propylene. Butyl iodide and aqueous ammonia at 160° yield only tributylamine, and the action of tributylamine on butyl iodide is strictly analogous to that which takes place with the corresponding propyl-derivatives. Tributylamine acts slowly on butyl chloride at 80°, but at 170° pure dibutylamine hydrochloride and butylene are obtained. Dibutylamine and butyl iodide in the cold yield dibutylamine hydriodide and free tributylamine; at a higher temperature, the reaction is analogous to that obtained with the chloride.

Isoamyl iodide and aqueous ammonia at 150° yield tetramylammonium iodide. Triamylamine acts slowly on amyl iodide in the cold, but at 150° triamylamine hydriodide and amylene are formed. At 200°, the reaction is very rapid, and the products are diamylamine hydriodide and amylene. With amyl chloride, a salt of triamylamine is formed at 170°, and undergoes no further alteration even at 210°. Diamylamine and amyl iodide yield diamylamine hydriodide, free triamylamine, and tetramylammonium iodide.

Capryl chloride with aqueous ammonia in equal molecular proportions at 170° yields monocaprylamine together with a small quantity of the diamine and caprylene. With twice the proportion of ammonia, the diamine is the chief product, and no caprylene is formed. Capryl iodide with an equivalent quantity of ammonia at 160° yields only monocaprylamine, either free or together with caprylene, the latter occupying at 120° a volume equal to half the volume of capryl iodide used.

Benzyl and metatolyl chlorides yield the tertiary amines almost exclusively, whilst cinnamyl chloride yields the secondary amine. The bases are obtained in the form of salts by the action of the corresponding alcoholic chlorides. The formation of a bivalent hydrocarbon is especially marked with styrolylamines, cinnamene being obtained in large quantity. It is identical with the synthetical cinnamene of Berthelot, and part of it is obtained in the form of metacinnamene.

Whether the products of these reactions are in the free state or in the form of salts is determined by the conditions of equilibrium between the rival attractions of the ammonia and the amines for the ethereal salt which is present, and the acid contained in this salt. The increasing complexity of the amines is the result of a series of successive transformations, a bivalent hydrocarbon being produced simultaneously. This last fact is in favour of the ethylene theory of the constitution of amines.

C. H. B.

Allyl-diguanidine and its Derivatives. By A. SMOLKA (*Monatsh.*, 8, 379—390).—*Allyldiguanidine copper sulphate*, $(C_5H_{10}N_5)_2Cu, H_2SO_4$, is obtained by dissolving dicyandiamide in aqueous copper sulphate and adding allylamine; the mixture is then heated for some hours at 100° . This salt is more soluble in alkaline solutions than in pure water; it separates from boiling solutions in carmine-red, anhydrous crystals, from cold solutions in pale rose-coloured, microscopic needles with 1 mol. H_2O . The other salts were made from the foregoing by double decomposition. The *chloride*, $(C_5H_{10}N_5)_2Cu, 2HCl + 2H_2O$, yields groups of rose-red crystals easily soluble in water to an amethyst-coloured solution. The *nitrate*, $(C_5H_{10}N_5)_2Cu, 2HNO_3$, forms dark-red crystals easily soluble in water. Other salts were prepared. Copper-allyldiguanidine, $(C_5H_{10}N_5)_2Cu$, was obtained by precipitating a boiling solution of the sulphate with soda. It crystallises in dark rose-red needles, sparingly soluble in cold, more soluble in boiling water. A solution of this base precipitates metallic hydroxides from solutions of metallic chlorides, the chloride described above remaining in solution. When heated above 130° , the base decomposes.

Allyldiguanidine sulphate, $(C_5H_{11}N_5)_2, H_2SO_4 + \frac{1}{2}H_2O$, was obtained by the action of hydrogen sulphide on the copper salt suspended in water. It crystallises in prisms, and is soluble in water, insoluble in alcohol. The *acid sulphate*, $C_5H_{11}N_5, H_2SO_4 + \frac{1}{2}H_2O$, crystallises in scales. The *chloride*, $C_5H_{11}N_5, HCl$, yields transparent prisms easily soluble in water and alcohol. It yields no precipitate with $PtCl_4$, nor with potassium tartrate. The *acid chloride*, $C_5H_{11}N_5, 2HCl$, forms small, transparent prisms easily soluble in water and alcohol. *Allyldiguanidine*, $C_2H_5N_5 \cdot C_3H_5$, was prepared by treating a solution of the

sulphate with the calculated quantity of barium hydroxide and also by the action of hydrogen sulphide on copper allyldiguanidine suspended in water. It forms a slightly crystalline, very hygroscopic mass, is strongly alkaline in character, displacing ammonia from its salts and absorbing carbonic anhydride from the air. When heated with potash and chloroform, it yields allylcarbamine (C_3H_5NC).

In chemical characteristics, the above copper compound somewhat resembles the alkaline earthy metals, the allyldiguanidine, the alkali metals and especially sodium.

L. T. T.

Isonitroso-compounds. By E. BECKMANN (*Ber.*, **20**, 2580—2585; compare Abstr., 1887, 826).—The intramolecular change which takes place when diphenylketoxime is treated with phosphorus pentachloride or with sulphuric acid, is also produced by hydrochloric acid, acetic chloride, acetic anhydride, and acetic acid.

When a cooled solution of diphenylketoxime in 10 parts of glacial acetic acid containing acetic anhydride is saturated with hydrogen chloride, and then heated at 100° , the oxime is completely converted into benzanilide; this is precipitated by sodium carbonate, and recrystallised from alcohol. Methylphenylketoxime when similarly treated yields acetanilide, which separates as hydrochloride on cooling the solution; the reaction takes place in the cold, but requires some days.

Methylpropylketoxime is converted by hydrochloric acid into the compound $NHPr \cdot CMeO, HCl$, and not into the compound $NHMe \cdot CPrO$. When diphenylketoxime is heated with acetic anhydride in presence of hydroxylamine hydrochloride at 150° , acetanilide and benzoic acid are formed. Methylphenylketoxime when heated with 10 parts of acetic anhydride for six hours at 100° , yields the compound $CMePh : N \cdot OAc$ (Rattner, *Ber.*, **20**, 506). This crystallises from light petroleum in forked needles melting at 55° .

Glacial acetic acid at 180° acts on diphenylketoxime with formation of benzanilide, acetanilide, and benzoic acid. Methylphenylketoxime is converted by hot glacial acetic acid into oily products; acetanilide is not formed.

N. H. M.

Oxidation by Means of Hydrogen Peroxide. By C. WURSTER (*Ber.*, **20**, 2631—2633).—The author showed previously (*Centr. für Physiol.*, 1887, 33) that organic acids are quickly oxidised by hydrogen peroxide to carbonic anhydride; the higher fatty acids and oils, cane- and grape-sugar, are rather stable towards hydrogen peroxide, whilst boiled starch is converted first into erythrodextrin and then into sugar.

Hydrogen peroxide (6 mols.) reacts with hydroxylamine sulphate at 40° with formation of sulphuric acid, nitric acid (2 mols.), and water (12 mols.). Hydroxylamine hydrochloride is similarly converted into hydrochloric and nitric acids and water. The yield is quantitative.

When an aqueous solution of phenol is treated with a hydroxylamine salt and hydrogen peroxide, nitrosophenol is formed.

Phenylhydrazine is converted by hydrogen peroxide into benzene and diazobenzeneimide. The production of benzene makes it pro-

bable that free diazobenzene is first formed in the oxidation of the hydrazine. N. H. M.

Isonitrosovaleric Acid and γ -Valeroximidolactone. By P. RISCHBIETH (*Ber.*, **20**, 2669—2673).—Isonitrosovaleric acid (Abstr., 1883, 1129) can readily be obtained by dissolving hydroxylamine hydrochloride (50 grams) and levulinic acid (83 grams) in a small quantity of water and adding a concentrated aqueous solution of sodium carbonate (38 grams); a separation of the acid immediately occurs, and this is purified by recrystallisation from water. The yield amounts to 90 per cent. of that theoretically possible. When treated with hydrogen chloride, the acid melts and absorbs the gas, and on warming the product, a sudden reaction occurs with the evolution of nitrogen, and production of a black residue. On oxidation with dilute nitric acid, a large volume of gas is evolved, and acetic and succinic acids are formed; the residue is, moreover, found to be free from nitrogen. If the acid (6 grams) is heated with sulphuric acid (10 grams) in a vacuum at 150° , succinic acid sublimes, and nitrogen is evolved; when, however, a much larger proportion of sulphuric acid (36 grams) is employed, and the heating is continued for 6 to 12 hours at 100° at the ordinary pressure, the elements of a molecule of water are withdrawn from the molecule of isonitrosovaleric acid, and the "inner anhydride," γ -valeroximidolactone, together with succinic acid, results.

γ -Valeroximidolactone, $\text{CMe} \begin{smallmatrix} \text{N} \text{---} \text{O} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{CO}$, crystallises from ether and water in long, white prisms; it melts at $69\text{--}70^{\circ}$ when slowly heated, and at a somewhat higher temperature when the heating is rapid, and boils at 232° without decomposition. When heated with aqueous alkalis, it yields the corresponding salts of isonitrosovaleric acid, but dilute sulphuric acid, hydrogen chloride, fuming hydrochloric acid, and ammonia are without action on it at 100° . On distillation with nitric acid (sp. gr. = 1.4), a distillate is obtained which contains in addition to unaltered lactone at least two distinct crystalline compounds; these have not yet been further examined. W. P. W.

New Source of Capric Acid. By A. BUISINE and P. BUISINE (*Compt. rend.*, **105**, 614—617).—Capric acid does not exist as such in suint, but an aqueous solution of suint undergoes fermentation under the influence of microbes, and the quantity of fatty acids and especially of capric acid is greatly increased, the proportion of the latter rising to 5 per cent.

The capric acid is separated by distillation, saponification, and subsequent fractionation, and is finally crystallised from boiling water. It forms a crystalline, buttery mass, with an odour of rancid butter, melts at 31° , is soluble in alcohol and ether, and is slightly soluble in boiling water, from which it crystallises in white needles. The barium salt is soluble in alcohol. C. H. B.

Linoleic Acid. By L. M. NORTON and H. A. RICHARDSON (*Ber.*, **20**, 2735—2736).—When endeavouring to dry linoleic acid at 100° in a

current of hydrogen, the authors found that a continued loss of weight occurred even after 28 hours, although no change in composition took place. Linoleic acid can be distilled without any appearance of decomposition at 290° under 89 mm. pressure, and a colourless product is obtained amounting to about three-fourths of the acid taken. This consists of an acid, $C_{20}H_{36}O_2$, which cannot again be distilled in a vacuum without decomposition; its sp. gr. is 0.9108 at 15°, and its vapour-density = 153.

Under similar conditions, ricinoleic acid yields an acid agreeing in composition with that just described. W. P. W.

Butanedicarboxylic Acid. By R. OTTO and A. RÖSSING (*Ber.*, **20**, 2736—2747).—By the reduction of dimethylmaleic acids, two butanedicarboxylic acids are obtained, the one, melting at 193—194°, which has been shown to be symmetrical dimethylsuccinic acid, the other, ethylmethylmalonic acid, melting at 118—120°. In this paper, the anhydrides of these acids are more particularly studied. The former on dry distillation yields an anhydride melting at 87°, previously described by Bischoff and Rach; but this substance on rehydration and crystallisation from the aqueous solution yields not only the original or symmetrical dimethylsuccinic acid, but also the above-mentioned isomeric ethylmethylmalonic acid. On the other hand, the symmetrical dimethylsuccinic acid, when treated with excess of acetic chloride, yields an anhydride isomeric with the above, which crystallises in rhombic tables melting at 38°; this on rehydration yields the original acid only.

Again the butanedicarboxylic or ethylmethylmalonic acid, melting at 121°, remains unaltered on dry distillation, but when treated with acetic chloride it yields an anhydride of the same melting point, 86—87°, and crystalline form as the former of the anhydrides mentioned above, but which, however, differs from it in yielding on rehydration the original acid only. V. H. V.

Distillation of Citric Acid with Glycerol. By P. DE CLERMONT and P. CHAUTARD (*Compt. rend.*, **105**, 520—523).—500 grams of crystallised citric acid mixed with 750 grams of ordinary glycerol of 28° are distilled in a glass retort of 3 litres capacity, and the product redistilled. The first fraction consists of about 250 grams of water containing a small quantity of acetaldehyde, &c.; some crystals also separate in the colder part of the apparatus. The mass then swells up, and the temperature must be reduced, but it is afterwards gradually raised until the distillation is complete. The distillate during this second stage consists of 650 to 700 grams of liquid. The total products of the decomposition are 950 grams of liquid, 30 grams of a bulky, carbonaceous residue, carbonic oxide and carbonic anhydride, and vapours of acetone and acetaldehyde. In addition to water containing small quantities of acetaldehyde, the only products in the distillate are unaltered glycerol and pyruvate or the pyruvic ether of glycidic acid, $MeCO \cdot COO \cdot CH_2 \cdot CH < \begin{smallmatrix} CH_2 \\ -O- \end{smallmatrix} >$, which is also obtained by the distillation of glycerol with tartaric acid or glyceric acid. Probably

the pyruvone is a product of the reaction between glycerol and glyceric acid, the latter being formed as an intermediate product.

The pyruvone thus obtained crystallises in large, prismatic needles, or tables, which melt at 82° and boil at 241° under a pressure of 764 mm.

C. H. B.

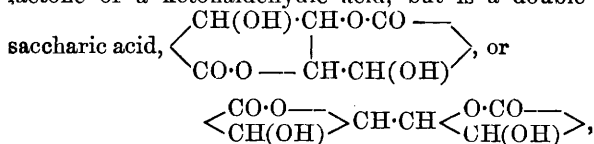
Double Lactone of Metasaccharic Acid. By H. KILIANI (*Ber.*, 20, 2710—2716).—The oxidation product of the lactone of arabinose-carboxylic acid (*Abstr.*, 1887, 465) dissolves readily in aqueous ammonia, and from the solution the *diamide* of metasaccharic acid, $C_6H_{12}O_6N_2$, separates as a white powder, consisting of microscopic, tabular, monoclinic crystals, which become yellow at 170° and melt at 189 — 190° with complete decomposition. The compound has a neutral reaction, and when heated at 100° with potassium hydroxide yields the potassium salt of metasaccharic acid as a colourless syrup; this becomes crystalline on stirring, and in aqueous solution does not reduce Fehling's solution.

On treatment with a cold solution of phenylhydrazine hydrochloride (1 part) and sodium acetate (1.5 part), in water (10 parts), the oxidation product yields the *monophenylhydrazide* of the lactone of metasaccharic acid, $C_{12}H_{14}O_6N_2$; this crystallises in colourless, microscopic scales with $\frac{1}{2}$ mol. H_2O , dissolves readily in hot water and alcohol, and when rapidly heated becomes yellow at 185° , and melts at 190 — 192° with decomposition. If the mixture with phenylhydrazine (which, to obtain the preceding compound is allowed to remain for 20 minutes for the crystallisation to take place) is at once poured into boiling water, the *diphenylhydrazide* of metasaccharic acid, $C_{18}H_{22}O_6N_4$, separates after 10 to 15 minutes in yellowish-white, microscopic scales, which become yellow at 210° , melt at 212 — 213° with decomposition, and are very sparingly soluble in boiling water and alcohol. The solution in concentrated sulphuric acid is coloured red or bluish-violet by ferric chloride.

When the oxidation product (12 grams) is dissolved in water (300 grams), treated with 3 per cent. sodium amalgam (200 grams), and dilute sulphuric acid added gradually so that the solution never becomes alkaline, allowed to remain five days with a further 200 grams of sodium amalgam, then treated with sulphuric acid and alcohol to free the product from sodium sulphate, and the mother-liquor evaporated, a syrup is obtained which still reduces alkaline copper solution, and from which mannite (2 grams) crystallises on standing over sulphuric acid. The strongly acid mother-liquor seems to consist of the lactone of a bibasic acid ($\frac{1}{2}$ metasaccharic acid), a strongly acid syrup having similar properties being also obtained by continued heating of the oxidation product with water, or by repeated evaporation of its aqueous solution.

The oxidation product of the lactone of arabinose-carboxylic acid dissolves in 18, not 8, parts of cold water (compare *loc. cit.*), and readily reduces alkaline copper solution. The aqueous solutions of its potassium and sodium salts, even in the absence of free alkali, become coloured intensely red on heating, or when allowed to evaporate spontaneously (*Ber.*, 20, 343). The author, however, concludes, from

the preceding experiments, that the oxidation product is not the lactone of a ketonaldehydic acid, but is a double lactone of meta-



which, on account of its peculiar constitution is very labile, and on treatment with alkalis even at the ordinary temperature undergoes molecular change, or perhaps reduction to an aldehyde-compound yielding mannite by the action of nascent hydrogen. W. P. W.

Thiohydantoin. By R. ANDREASCH (*Monatsh.*, 8, 407—424).—Loven has recently shown (*Abstr.*, 1885, 241) that a methylene-group situated between a carbonyl-group and a sulphur-atom possesses similar properties to the methylene-group in ethyl malonate and acetoacetate. With the object of ascertaining whether this is the case in hydantoin, the author has prepared the disilver-derivative, and from that the dimethyl-compound.

Disilverthiohydantoin, $\text{Ag}_2\text{C}_3\text{N}_2\text{H}_2\text{SO}$, was obtained by adding a warm aqueous solution of thiohydantoin to ammoniacal silver nitrate. It forms a white, granular substance, sparingly soluble in nitric acid, insoluble in ammonia. It blackens when exposed to light. When treated with methyl iodide, the silver compound yields β -dimethylthiohydantoin, $\text{NH} : \text{C} \left\langle \begin{array}{c} \text{S} \cdot \text{CMe}_2 \text{ ---} \\ | \\ \text{NH} \cdot \text{CO} \end{array} \right\rangle$. This substance is easily soluble in water, sparingly in cold alcohol, crystallises in hexagonal scales, melts at 114° , and decomposes at a slightly higher temperature. When oxidised in hydrochloric solution by barium chlorate, carbonic anhydride and mercaptan are evolved, and the residue is found to contain carbamide, and a mixture of barium salts which cannot be separated, but one of which seems to be barium methylsulphonate. When heated with barium hydroxide, the hydantoin yields cyanamide and some sulphur compounds which could not be isolated.

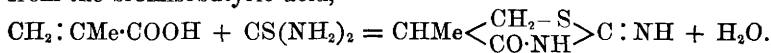
With the aim of determining the constitution of the above compound, the author attempted to prepare the two isomeric dimethylhydantoins in other ways. α -Dimethylthiohydantoin,



may be prepared by heating together dimethylthiocarbamide and chloroacetic acid in aqueous solution. It is easily soluble in water, alcohol, ether, and carbon bisulphide, crystallises in long, thin, colourless prisms, melts at 71° , and boils at a rather higher temperature. It volatilises slowly at ordinary temperatures. It has an odour somewhat resembling that of nicotine. When heated with aqueous alkalis, it yields thioglycollic acid. The *isonitroso*-derivative, $\text{C}_5\text{H}_7\text{N}_3\text{SO}_2$, yields yellowish scales melting at 220° . *Imidocarbaminethioisobutyric anhydride*, $\text{C}_6\text{N}_2\text{H}_4\text{SO}$, was prepared by heating together thiocarbamide and α -bromisobutyric acid. It crystallises in plates, is easily

soluble in alcohol and boiling water, sparingly in cold water, and melts at 242° . When oxidised with nitric acid, this substance yields carbamide and *sulphoisobutyric acid*, $\text{SO}_3\text{H}\cdot\text{C}_3\text{H}_6\text{COOH}$, which forms a *barium salt*, $\text{BaC}_4\text{H}_6\text{SO}_5 + 4\text{H}_2\text{O}$, crystallising in needles, easily soluble in water, insoluble in alcohol. The *sodium salt*, $\text{Na}_2\text{C}_4\text{H}_6\text{SO}_5 + \frac{1}{2}\text{H}_2\text{O}$, forms glistening needles easily soluble in water, insoluble in alcohol. The same sulpho-acid is obtained by the action of chloro-sulphonic acid on isobutyric acid. The action of ammonium sulphite on α -bromisobutyric acid produces, however, an isomeric sulpho-acid, yielding an easily soluble *barium salt*, $\text{BaC}_4\text{H}_6\text{SO}_5 + 2\text{H}_2\text{O}$, crystallising in needles.

It is thus clear that this imido-anhydride is not identical with the β -dimethylthiohydantoin, as the author had anticipated. As it was possible that in the formation of the imido-anhydride a transformation from the iso- to the normal butyric series had occurred, the author prepared *imidocarbaminethiobutyric anhydride*, $\text{NH}:\text{C} \begin{smallmatrix} \text{S}\cdot\text{CHEt} \\ \text{NH}\cdot\text{CO} \end{smallmatrix}$, by the action of α -bromobutyric acid on thiocarbamide. This crystallises in short, thick needles, easily soluble in boiling water, and melts at 200° . It is not identical with the compound obtained from isobutyric acid. The constitution of the latter is therefore still doubtful, but its formation may perhaps be due to the action of thiocarbamide on the methacrylic acid formed by the elimination of hydrogen bromide from the bromisobutyric acid,



The constitution of the β -compound would then be correctly expressed by the formula given above.

Thiohydantoin when treated with benzaldehyde yields *amidinethiocinnamic (benzylidenethiohydantoic) acid*, $\text{NH}:\text{C}(\text{NH}_2)(\text{COOH})\cdot\text{CHPh}$; this forms white, microscopic needles, insoluble in water, soluble in alcohol. Similar acids seem to be produced with other aldehydes.

Several salts of thiohydantoin are described. The *sulphate*, $(\text{C}_3\text{H}_4\text{N}_2\text{SO})_2\cdot\text{H}_2\text{SO}_4$, forms plates soluble in water; the *nitrate*, flat needles or prisms; the *oxalate*, $\text{C}_3\text{H}_4\text{N}_2\text{SO}\cdot\text{C}_2\text{H}_2\text{O}_4 + \text{H}_2\text{O}$, prisms; the *picrate* yellow, microscopic needles.

Thiohydantoin is best prepared as follows: 50 grams of thiocarbamide is dissolved in $\frac{1}{2}$ litre water, and 62 grams of chloroacetic acid dissolved in 50 c.c. of water added. The whole is heated at 80 – 90° until reaction has ceased, and when cold it is gradually neutralised with soda, care being taken never to let the solution become alkaline.

L. T. T.

Orthothioxen and Orthothiophendicarboxylic Acid. By W. GRÜNEWALD (*Ber.*, **20**, 2585–2587).—Orthothioxen (Paal, *Abstr.*, 1887, 1101) is prepared by distilling an intimate mixture of 10 grams of β -methyllevulinic acid and 17 grams of phosphorus trisulphide in a capacious retort. 250 grams of methyllevulinic acid yielded 150 grams of pure product. It is a colourless, strongly refractive oil, having an odour of petroleum; it boils at 136 – 137° (corr.). Sp. gr. at $21^{\circ} = 0.9938$. When treated with 1 per cent. solution of potassium permanganate, a monocarboxylic acid only is formed; this melts at 134.5° .

Orthothiophendicarboxylic acid, $C_4SH_2(COOH)_2$, is obtained by the action of 1 per cent. permanganate solution on the monocarboxylic acid; the product is steam-distilled to remove unchanged monocarboxylic acid. It crystallises in long needles which do not melt at 260° , but decompose at a higher temperature. When heated with resorcinol at 200° , a product is obtained which dissolves in strong aqueous alkali with dark-red coloration; the colour changes to yellow on diluting with water; the solution then shows a yellowish-green fluorescence. The *silver salt* forms white flakes insoluble in water; the *barium salt* separates in colourless crystals, readily soluble in hot water. The dimethyl salt crystallises from alcohol in colourless plates melting at 59.5° .
N. H. M.

Action of Carbonic Anhydride on Aromatic Amines. By A. DITTE (*Compt. rend.*, 105, 612—614).—When an aniline salt is mixed with an aqueous solution of a normal or hydrogen carbonate, carbonic anhydride is given off, and aniline separates in the free state, no aniline carbonate being formed. Carbonic anhydride is not soluble in aniline, and does not combine with it under ordinary pressure even at -8° , the temperature at which aniline solidifies.

If, however, dry carbonic anhydride and aniline are compressed in a Cailletet's apparatus, the aniline dissolves the carbonic anhydride, increasing to about twice its original volume, and a limpid layer of the liquefied gas swims on the surface of the solution and volatilises at 15° under a pressure of 40 atmos. If the compressed liquid is cooled to $8-10^\circ$, it crystallises in transparent, white needles, and when the aniline and carbonic anhydride are in equal molecular proportions, solidification is complete. When the carbonic anhydride is in excess, it forms a layer above the crystals. When aniline is in excess, it does not at once dissolve the carbonic anhydride, and the two liquids form distinct layers, but on gentle agitation the carbonic anhydride is dissolved, and crystallisation takes place at 8° . It is evident that carbonic anhydride and aniline combine in equal molecular proportions to form a compound which crystallises at 8° , and is liquid or remains in superfusion at 10° , and decomposes when the pressure is released. The tension of dissociation at different temperatures is as follows:—

Temperature	0°	2°	5°	7°
Pressure in atmos.	6	9	17	28

Orthotoluidine behaves in a precisely similar manner, and the compound crystallises in brilliant, white needles. The behaviour of metaxylidene is similar in that the two liquids mix, but no crystals form even at -12° .

Pyridine and its homologues show no tendency to combine with carbonic anhydride; the two liquids do not mix.
C. H. B.

Benzylidene Compounds. By L. KOHLER (*Annalen*, 241, 358—362).—An alcoholic solution of benzylideneparatoluidine is converted into benzylparatoluidine by the action of sodium amalgam. The
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base distils at 312—313°, and solidifies in the course of several weeks. It is freely soluble in alcohol and ether. The hydrochloride is soluble in alcohol and in hot benzene, and the sulphate is soluble in water. The nitroso-compound melts at 53°.

Benzyl-β-naphthylamine crystallises in prisms, and melts at 68°. The nitroso-derivative forms yellow needles, soluble in alcohol, ether, benzene, and light petroleum. It melts at 111—112°.

Benzylamidodimethylaniline, prepared from the condensation-product of benzaldehyde and amidodimethylaniline, melts at 48°, and distils without decomposition. The *nitrosamine* is deposited from alcohol in yellow needles. It melts at 127—128° with decomposition.

W. C. W.

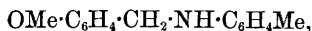
Reduction Products of Benzylidene Compounds. By O. FISCHER (*Annalen*, **241**, 328—331).—The author has previously pointed out (Abstr., 1886, 546) that 3 per cent. sodium amalgam reduces a solution of hydrobenzamide in absolute alcohol to dibenzylamine and monobenzylamine; ammonia and toluene are always liberated during the reaction. Under similar treatment, benzylideneaniline is converted into benzylaniline.

The salt which is deposited when nitrosobenzylaniline is treated with alcoholic hydrogen chloride is a mixture of benzylaniline hydrochloride and benzylidene aniline.

W. C. W.

Hydroxybenzylidene Compounds. By O. EMMERICH (*Annalen*, **241**, 343—358).—*Orthohydroxybenzylaniline*, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NHPh}$, is obtained by the action of sodium amalgam on a solution of hydroxybenzylideneaniline in absolute alcohol. It melts at 106°, and is soluble in alcohol and ether. The sulphate and hydrochloride are freely soluble in water. The platinochloride forms reddish-yellow needles, melting at 184° with decomposition. A tetranitro-derivative, $\text{C}_{13}\text{H}_9\text{NO}(\text{NO}_2)_4$, is formed when the base is treated with a mixture of sulphuric and nitric acids. It melts at 66° with decomposition, and is soluble in alcohol, acetic acid, and light petroleum.

Orthohydroxybenzylparatoluidine, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, obtained by the reduction of the hydroxybenzylideneparatoluidine, crystallises in white plates and needles, and melts at 116°. It is soluble in alcohol and ether. The sulphate and hydrochloride dissolve freely in water. The platinochloride crystallises in needles. The tetranitro-derivative forms yellow needles, soluble in alcohol, benzene, and acetic acid. It melts at 168°. By the action of methyl iodide, the base is converted into *orthomethoxybenzylparatoluidine*,



a crystalline compound melting at 110°, and soluble in alcohol, ether, and benzene.

Orthodihydroxydibenzylamine is prepared by the action of sodium amalgam on an alcoholic solution of hydrosalicylamide. It crystallises in needles, melts at 170°, and dissolves freely in ether, alcohol, benzene, and light petroleum. The sulphate, nitrate, and hydro-

chloride are soluble in water. The platinumchloride crystallises in needles, and is soluble in water.

The condensation compound of salicylaldehyde and β -naphthylamine yields on reduction *orthohydroxybenzyl- β -naphthylamine*,



a crystalline substance melting at 147° . It is soluble in alcohol, ether, benzene, and light petroleum. The alcoholic solution exhibits a reddish-violet fluorescence. The sulphate is liquid, and the platinumchloride crystallises with difficulty.

Orthohydroxybenzyl- β -naphthylnitrosamine melts at 165° with decomposition. On exposure to the air, the compound decomposes spontaneously at the ordinary temperature. It is soluble in alcohol and ether. *Orthomethoxybenzyl- β -naphthylamine* crystallises in needles, melts at 92° , and dissolves freely in alcohol and ether.

Parahydroxybenzylaniline, prepared from parahydroxybenzylideneaniline, is soluble in alcohol and ether. It melts at 208° , and forms a crystalline platinumchloride.

Parahydroxybenzyltoluidine melts at 186° . *Parahydroxybenzyl- β -naphthylamine* melts at 117° . The sulphate is soluble in alcohol, but almost insoluble in water. The *nitrosamine* melts at 142° , and dissolves in alcohol and ether. It is unstable.

W. C. W.

Anisylamines. By O. J. STEINHART (*Annalen*, **241**, 332—343).—A solution of anishydramide in absolute alcohol is converted into a mixture of mono- and di-anisylamine by the action of sodium amalgam at the ordinary temperature. *Dianisylamine*, $\text{NH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_2$, forms white, needle-shaped crystals soluble in alcohol and ether. It melts at 34° , and decomposes on distillation. The *hydrochloride* is soluble in alcohol, and crystallises in flat prisms. It melts at 243° . The platinumchloride is crystalline but unstable. The *nitroso*-derivative, $(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2)_2\text{N}\cdot\text{NO}$, crystallises in needles, and melts at 80° . *Anisylamine* is a colourless liquid boiling at 220 — 223° . It is miscible with alcohol, ether, and water, and it absorbs carbonic anhydride from the air. It can be separated from dianisylamine by its volatility in a current of steam. The hydrochloride forms white plates which are freely soluble in water, and melt at 230° . The platinumchloride crystallises in pale-yellow, glistening needles. It melts at 210° .

Anisylaniline, $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NHPh}$, prepared from anishydranilide, crystallises in prisms, and dissolves freely in the usual solvents. It melts at 64.5° , and forms a crystalline hydrochloride, sulphate, and platinumchloride. The *nitroso*-derivative melts at 104° . It crystallises in prisms, and is soluble in alcohol.

Anishydroparatoluide, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NC}_6\text{H}_4\text{Me}$, forms white needles, and melts at 92° . *Anisylparatoluidine*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{C}_6\text{H}_4\text{Me}$, forms white prisms, melting at 68° . It is soluble in all the usual solvents with the exception of water. The hydrochloride and platinumchloride are crystalline, but the salts have a tendency to decompose when their solutions are evaporated. The *nitrosamine* melts at 108° .

Anisaldehyde and orthotoluidine condense, forming anishydrortho-

toluide, which yields orthotoluylanisylamine on reduction. The base melts at 55°. The nitrosamine is an oily liquid.

Anisylidenenaphthylamine(β), $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NC}_{10}\text{H}_7$, crystallises in plates, and melts at 98°. *Anisyl- β -naphthylamine* is soluble in alcohol, benzene, and in light petroleum. It melts at 101°. The salts are sparingly soluble in water, and are rather unstable. The nitrosamine melts at 133°, and crystallises in plates. *Anisylidenedimethylparaphenylenediamine* forms greenish-yellow needles. It melts at 148°, and yields on reduction *anisyl dimethylparaphenylenediamine*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$. This base crystallises in plates, and melts at 104°. The alcoholic solution decomposes on exposure to the air, and the nitroso-compound is unstable.

W. C. W.

Salts of Picramic Acid. By A. SMOLKA (*Monatsh.*, **8**, 391—398).—The salts of this acid having been but little studied, the author has prepared and examined a number of them. In some cases they were obtained by the direct action of picramic acid on the metallic carbonate, in others by double decomposition. The following table shows the results obtained:—

Formula of salt.	Description.	Ratio of solubility in water.		Temperature of decomposition.
		I. Boiling.	II. Cold.	
$\text{NaC}_6\text{H}_4\text{N}_3\text{O}_5 + \text{H}_2\text{O} \dots$	Dark red crystals	1:48·6 at 15·5°	freely	about 150°
$\text{Mg}(\text{C}_6\text{H}_4\text{N}_3\text{O}_5)_2 + 3\text{H}_2\text{O}$	Dark reddish-brown scales	1:17·9 „ 17·0	freely	140
$\text{Zn}(\text{C}_6\text{H}_4\text{N}_3\text{O}_5)_2 + \text{H}_2\text{O} \dots$	Yellow, microscopic needles	1:5890 „ 23·0	1:1842	140–150°
$\text{Cd}(\text{C}_6\text{H}_4\text{N}_3\text{O}_5)_2 + \text{H}_2\text{O} \dots$	Greenish-yellow needles	1:1215 „ 23·0	1:318	140°
$\text{Hg}_2(\text{C}_6\text{H}_4\text{N}_3\text{O}_5)_2 \dots \dots$	Scarlet, microscopic crystals	1:21010 „ 17·5	1:12481	120
$\text{Hg}(\text{C}_6\text{H}_4\text{N}_3\text{O}_5)_2 + \text{H}_2\text{O} \dots$	Dull yellow, microscopic needles	1:3172 „ 18·0	1:1151	140–145°
$\text{Pb}(\text{C}_6\text{H}_4\text{N}_3\text{O}_5)_2 \dots \dots$	Small, reddish-brown needles	1:2632 „ 20·5	1:1494	140–150
$\text{Mn}(\text{C}_6\text{H}_4\text{N}_3\text{O}_5)_2 + 2\text{H}_2\text{O}$	Dark steel-green needles	1:97·5 „ 19·0	freely	150°
$\text{Co}(\text{C}_6\text{H}_4\text{N}_3\text{O}_5)_2 \dots \dots$	Greenish-yellow, amorphous powder	insoluble	1:3292	140
$\text{Ni}(\text{C}_6\text{H}_4\text{N}_3\text{O}_5)_2 \dots \dots$	Dark olive-green, amorphous powder	insoluble	1:3532	140–145°

If the salt is heated slowly, the decomposition takes place quietly, but if rapidly, explosions occur, especially with the sodium and lead salts. The aqueous solutions vary in colour from pale orange to dark blood-red.

L. T. T.

Chlorine and Bromine-derivatives of Citraconanil. By T. MORAWSKI and J. KLAUDY (*Monatsh.*, **8**, 399—406).—*Citraconparachloranil*, $C_5H_4O_2 : N \cdot C_6H_4Cl$, is formed (together with chloranilines) when a stream of chlorine is passed into water in which finely-divided citraconanil is suspended. It crystallises in white, glistening needles, soluble in alcohol and melting at 114.5° . With care it may be sublimed in long, glass-like needles. When heated with ammonia, it yields parachloraniline and citraconic acid, showing the correctness of the above formula.

When bromine acts on citraconil, *bromocitraconparabromanil*, $C_5H_3BrO_2 : N \cdot C_6H_4Br$, is formed. This crystallises in white, shining needles, soluble in alcohol and melting at 178° . It can be sublimed, but decomposes if heated rapidly. When heated with ammonia, parabromaniline is formed, together with hydrogen bromide, much resinous matter, and an acid of the formula $C_7H_3BrO_4$. This acid yields a silver salt, $Ag_2C_7H_3BrO_4$, crystallising in prisms, and a lead salt, $PbC_7H_3BrO_4$, forming microscopic crystals. It appears, therefore, that the original bromo-derivative contained one bromine-atom in the citraconic nucleus, and that when heated with ammonia this nucleus is converted into a higher brominated homologue of the citraconic series, together with other bye-products.

When only enough bromine is employed for the formation of *citraconparabromanil*, white, crystalline needles melting at about 118° were obtained, but this compound has not yet been obtained in a pure state.

L. T. T.

Action of Phenylhydrazine on Ethyl Chloracetoacetate. By G. BENDER (*Ber.*, **20**, 2747—2752).—Ethyl chloracetoacetate reacts with phenylhydrazine in ethereal solution to form a compound, $C_{12}H_{14}N_2O_2$; it is probable that a hydrazine-derivative,



is at first formed, which is subsequently converted into a compound, $NPh : N \cdot CHMe \cdot CHCl \cdot COOEt$, and finally by abstraction of the elements of hydrogen chloride into $NPh : N \cdot CMe : CH \cdot COOEt$, or ethylic β -phenylazocrotonate. This substance crystallises in long, red needles, melting at 50.5° , very soluble in alcohol; on saponification, it yields a potassium salt, $NPh : N \cdot CMe : CH \cdot COOK$, which forms reddish-yellow scales, very soluble in water, insoluble in alcohol. The salt on acidification yields the corresponding anhydride as a brownish-yellow powder, whose purification presents considerable difficulty. Ethylic β -phenylazocrotonate when reduced yields phenylmethylpyrazolone and its first oxidation product or its bis-derivative, together with a substance not further examined. The bis-derivative yields with bromine a compound, $C_{20}H_{21}N_4O_4Br$, which crystallises in colourless needles, melting at 217° with decomposition. α -Naphthylamine with ethylic chloracetoacetate yields a compound, $C_{16}H_{16}NO_2Cl$; this crystallises in colourless prisms, melting at 75° ; its formation is due to a change analogous to the first of the reactions given above in the case of phenylhydrazine.

V. H. V.

Isomeric Phthalophenylhydrazines. By G. PELLIZARI (*Gazzetta*, 17, 278—285).—The author has previously described two isomeric phthalyl-derivatives of phenylhydrazine obtained by the action of this base on phthalimide and phthalic anhydride respectively (Abstr., 1886, 125). To the former, melting at 179°, the constitution $\text{NPh}\cdot\text{N} < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{C}_6\text{H}_4$, to the latter, melting at 210°, the constitution $< \begin{smallmatrix} \text{NPh}\cdot\text{CO} \\ \text{NH}-\text{CO} \end{smallmatrix} > \text{C}_6\text{H}_4$ was assigned. If these formulæ are correct, a methyl-derivative of the former, or anilophthalimide, on separation of the phthalyl grouping, should yield a symmetrical methylphenylhydrazine, $\text{NPhMe}\cdot\text{NH}_2$, that of the latter, or phthalophenylhydrazine, the symmetrical derivative, $\text{NPh}\cdot\text{NHMe}$. Phthalophenylhydrazine, heated with methyl iodide and alcohol, yields a methyl-derivative, crystallising in long, yellowish-white prisms, which melt at 125° without decomposition; this is decomposed by concentrated hydrochloric acid, yielding methylphenylhydrazine, $\text{NPh}\cdot\text{NHMe}$. The constitution of the isomeride has previously been proved by Hötte, but in answer to his criticisms (Abstr., 1887, 770) it is shown that phthalic anhydride and phenylhydrazine, reacting in molecular proportions, give either anilophthalimide or phthalophenylhydrazine, according to the temperature; at ordinary temperatures, phenylhydrazine-phthalic acid is at first formed, which on subsequent heating yields anilophthalimide; if, however, the reaction proceeds at 163°, the melting point of the acid, at which temperature it is unstable, phthalophenylhydrazine is formed in the greater proportion.

V. H. V.

Dyes from Aniline Chromates. By S. GRAWITZ (*Compt. rend.*, 105, 576—577).—A question of priority and patent right.

Azophenine. By O. N. WITT (*Ber.*, 20, 2659—2660).—A reply to Fischer and Hepp (Abstr., 1887, 1105), in which the author points out that the constitutional formula proposed by them is inadmissible, since azophenine does not form an acetyl-derivative when heated with acetic anhydride, and yields a considerable quantity of aniline on treatment with tin and hydrochloric acid. On these grounds, the author adheres to his published views on the constitution of azophenine (Abstr., 1887, 821).

W. P. W.

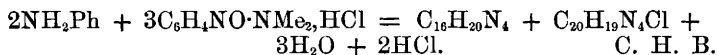
Substituted Safranines. By P. BARBIER and L. VIGNON (*Compt. rend.*, 105, 670—672).—Paranitrosodimethylaniline has no action on aniline at the ordinary temperature in presence of water, glacial acetic acid, or an excess of aniline, but at 80° there is an extremely violent reaction.

If equal molecular proportions of aniline and paranitrosodimethylaniline are dissolved in eight times their weight of ethyl alcohol of 92°, and heated on a water-bath, a reaction takes place at 80°, with considerable development of heat, and is complete in about three hours. When the liquid is cooled, a solid separates, which is washed with dilute hydrochloric acid, and then crystallised from boiling toluene. *Tetramethyldiamido-azobenzene* is thus obtained in brilliant, brown,

crystalline plates, which melt imperfectly at 218—220° without volatilisation, and when reduced with zinc and sulphuric acid, yield dimethylparaphenylenediamine in almost theoretical quantity. It is almost insoluble in water, and only slightly soluble in dilute acids, but dissolves in concentrated acids forming deep red solutions.

The alcoholic liquid separated from the tetramethyldiamido-azobenzene has a deep, violet-red colour, and when evaporated leaves a viscid residue, which dissolves almost completely in water. When this solution is mixed with sodium carbonate, a precipitate is formed, and if the filtrate is mixed with sodium chloride, dimethylphenosafranine separates, and is purified by repeating the treatment with sodium carbonate and chloride.

The equation representing the reaction is—



Action of Acid Amides on Bromacetophenones. By M. LEWY (*Ber.*, 20, 2576—2580).—When bromacetophenone is heated with acetamide (2 parts) at 120—130°, for one hour, a *base*, $\text{C}_{10}\text{H}_9\text{NO}$, is obtained. This forms long, colourless needles, readily soluble in alcohol and ether; it melts at 45°, and boils at 241—242°; it has slightly basic properties. The hydrochloride, $\text{C}_{10}\text{H}_9\text{NO}\cdot\text{HCl}$, crystallises in small needles; when treated with an excess of hydrogen chloride, it yields a heavy, fuming oil, possibly an acid salt. The *platinochloride*, $(\text{C}_{10}\text{H}_9\text{NO})_3\cdot\text{H}_2\text{PtCl}_6 + 2\text{H}_2\text{O}$, separates in dense, yellow flakes, consisting of orange-coloured needles, which melt at 130—140° with decomposition. The *sulphate* forms white, lustrous plates, which decompose in contact with water. The *picrate* crystallises in lemon-coloured needles, melting at 133—134°.

The *formamide base*, $\text{C}_9\text{H}_7\text{NO}$, prepared by heating bromacetophenone with formamide, is a thick, colourless oil, which becomes yellow when exposed to air; it solidifies when cooled with a freezing mixture, melts at 6°, and boils at 220—222°. The *hydrochloride* melts at 80°. The *platinochloride* (with 2 mols. H_2O) crystallises in slender, yellow needles. The *benzamide base*, $\text{C}_{15}\text{H}_{11}\text{NO}$, is prepared by heating bromacetophenone and benzamide at 140—150°; the product is extracted several times with boiling water, and the residue fractionally distilled. It crystallises from alcohol in large, colourless plates, readily soluble in the usual solvents, melts at 102—103°, and boils at 338—340°. The hydrochloride crystallises in slender, matted needles; it is slowly decomposed by boiling water.

N. H. M.

Isonitroso-compounds: Isobenzaldoxime. By E. BECKMANN (*Ber.*, 20, 2766—2768).—When benzaldoxime is mixed with sulphuric acid in presence of ice, a solid, white substance separates out under certain conditions; sometimes an oil is obtained. The former, probably a polymeride of benzaldoxime, crystallises in glistening needles, melting at 128—130°; it is distinguishable from benzamide by its crystalline form. The oil is benzaldehyde, produced by the re-forma-

tion of the oxime and its subsequent decomposition by the acid present. V. H. V.

Condensation of Cinnamic Acid with Gallic Acid. By E. JACOBSEN and P. JULIUS (*Ber.*, 20, 2588—2589).—*Styrogallol*, $C_{16}H_{10}O_6$, is prepared by heating cinnamic acid (10 parts), gallic acid (12 parts), and sulphuric acid (150 parts) at 45—55°, for two to three hours. The product is poured into water, filtered, and the precipitate washed with slightly acidified boiling water. It crystallises in bright-yellow, microscopic needles, which do not melt at 350°; it is very sparingly soluble, except in boiling alcohol, aniline, and glacial acetic acid, and sublimes when carefully heated in large, yellow, lustrous needles. Alkalis dissolve it with green colour, which changes to blue, and then red, when the solution is heated. The solution in sulphuric acid is yellowish-red. When oxidised with dilute nitric acid, it yields a large amount of phthalic acid. The *triacetyl-derivative*, $C_{22}H_{16}O_8$, crystallises in pale-yellow needles. With mordants, styrogallol yields shades similar to those obtained with nitroalizarin. N. H. M.

Paradiphenoldicarboxylic Acid. By R. SCHMITT and C. KRETZSCHMAR (*Ber.*, 20, 2703—2704).—*Paradiphenoldicarboxylic acid*, $COOH \cdot C_6H_3(OH) \cdot C_6H_3(OH) \cdot COOH$, is obtained when sodium paradiphenol is heated in an autoclave with liquid carbonic anhydride at 200° for nine hours, and the resulting product is treated with an acid. It crystallises in small, microscopic needles, melts at 131° with the evolution of carbonic anhydride, is not volatile with steam, has a slightly bitter taste, and is readily soluble in ethyl and methyl alcohol and in ether, sparingly soluble in water (100 c.c. of water at 15° dissolving 0.0052 gram of the acid), and insoluble in benzene and chloroform. Suspended in water, it is coloured bluish-violet with ferric chloride, the colour changing to a dull brown on heating, whilst the sodium salt when similarly treated yields a deep blue solution, from which indigo-blue flocks separate. W. P. W.

Orthamidotriphenylmethane. By O. FISCHER and A. FRÄNKEL (*Annalen*, 241, 362—368).—The preparation of diphenylquinolylmethane has been previously described by the authors (*Abstr.*, 1886, 561). The sulphate and picrate are precipitated on the addition of sulphuric or picric acid to alcoholic solutions of the base. The nitro-derivative melts at 213° with decomposition, and the amido-compound on oxidation forms a violet-coloured solution.

Triphenylmethaneorthocarboxylic acid is prepared by slowly adding a solution of the hydrochloride of the diazo-compound of amidotriphenylmethane to a solution of potassium cyanide and copper sulphate at 90°. The crude product is saponified with alcoholic potash, and the acid precipitated from the aqueous solution of the potassium salt by hydrochloric acid. Alcohol, ether, acetic acid, and benzene dissolve the acid freely. It melts at 162° and volatilises without decomposition; it is identical with the acid Baeyer (*Abstr.*, 1880, 650) obtained from phthalophenone.

Orthohydroxytriphenylmethane is formed by passing air through a

solution of diazoamidotriphenylmethane sulphate, and boiling the product in a current of carbonic anhydride. It is soluble in alcohol and ether, and melts at 118°.

The acetic derivative of amidotriphenylmethane melts at 168—169°, and is freely soluble in alcohol, benzene, and acetic acid. The *thiocarbamide* melts at 123°, and dissolves readily in ether, carbon bisulphide, and hot alcohol.

W. C. W.

Two Dihydroxynaphthalenes. By A. EMMERT (*Annalen*, **241**, 368—373).— β -Naphthol yields two sulphonic acids on treatment with sulphuric acid, and each acid is converted into a dihydroxynaphthalene by fusion with potash.

β - β -Dihydroxynaphthalene melts at 215—216°, and dissolves freely in alcohol and ether. Ferric chloride produces a yellowish-white precipitate. At 120° alcoholic potash and ethyl iodide convert the dihydroxynaphthalene into an ethyl ether, $C_{10}H_6(OEt)_2$. It forms silky plates and melts at 162°. The *diacetate*, $C_{10}H_6(OAc)_2$, melts at 175°.

β - α -Dihydroxynaphthalene is soluble in alcohol, ether, benzene, and water. It melts at 178°, and gives a blue precipitate with ferric chloride. The diethyl ether crystallises in prisms, melting at 67°, and the diacetate forms rhombic plates and melts at 108°.

W. C. W.

Derivatives of Di- β -naphthylamine. By C. RUS (*Ber.*, **20**, 2618—2628).—Crude di- β -naphthylamine is purified by distillation and crystallisation from benzene; it melts at about 471°.

Methyldi- β -naphthylamine, $NMe(C_{10}H_7)_2$, is prepared by heating di-naphthylamine and methyl iodide (equal molecular weights) for five hours at 150°, and crystallises from alcohol in nearly colourless needles melting at 139—140°. It dissolves rather readily in warm alcohol, glacial acetic acid, benzene, and ether, and is almost insoluble in light petroleum. The alcoholic solution shows a bluish-violet fluorescence. It is insoluble in dilute mineral acids; the *hydrochloride* forms slender, lustrous crystals, which decompose quickly in presence of water. The solution in strong sulphuric acid is yellow, and acquires an intense brown colour on addition of a trace of a nitrite or nitrate.

Ethyldi- β -naphthylamine, $NEt(C_{10}H_7)_2$, crystallises in almost colourless prisms melting at 231°; it resembles the methyl compound in solubility; the *hydrochloride* is a white, crystalline powder.

Methyl di- β -naphthylcarbamate, $N(C_{10}H_7)_2COOMe$, is obtained by heating di- β -naphthylamine and methyl chloroformate (equal weights) at 150—160° for two and a half hours. It crystallises from alcohol in slender, white needles, melting at 113—114°, dissolves readily in alcohol, ether, and benzene. It crystallises from benzene with $\frac{1}{2}$ mol. C_6H_6 . It distils almost without decomposition.

Tetrabromodi- β -naphthylamine, $C_{20}H_{11}Br_4N$, is prepared by the action of bromine (4 mols.) on a well-cooled solution of di- β -naphthylamine in glacial acetic acid. It crystallises in long, white, matted needles, which melt at 245—246°. It dissolves rather readily in hot benzene and cumene, very sparingly in ether, light petroleum, and alcohol.

It is not attacked by boiling concentrated aqueous potash; bromine does not act on it.

Octobromodi-β-naphthylamine, $C_{20}H_7Br_8N$, is formed when β-dinaphthylamine, as dust, is added to an excess of bromine in presence of aluminium bromide. The product is stirred well, and the yellow precipitate, after being treated with alkali and with boiling hydrochloric acid to remove adhering bromine and aluminium, is crystallised from cumene. It forms slender, white needles, which melt at about 300°, and dissolve readily in boiling nitrobenzene, less in boiling cumene; in other solvents it is sparingly or not at all soluble.

Nitrosodi-β-naphthylamine, $NO \cdot N(C_{10}H_7)_2$, is prepared by adding the calculated amount of sodium nitrite dissolved in a little water to a mixture of alcohol and sulphuric acid containing di-β-naphthylamine in the form of dust. It crystallises from benzene in groups of white needles, melting at 139–140°, sparingly soluble in alcohol, readily in benzene.

Dinitrodi-β-naphthylamine, $C_{20}H_{13}N(NO_2)_2$, is formed when strong nitric acid is slowly added to a cooled solution of the amine in glacial acetic acid; it separates after some time as a yellow powder. It crystallises in yellowish-red needles, melting at 224–225°, readily soluble in boiling cumene, less soluble in benzene, and almost insoluble in alcohol and ether.

Tetranitrodi-β-naphthylamine, $C_{20}H_{11}N(NO_2)_4$, is obtained by gradually adding nitric acid (3 parts) mixed with glacial acetic acid to a solution of dinaphthylamine (1 part), in glacial acetic acid. It crystallises from nitrobenzene in grains, which melt at 285–286°, and detonate when more strongly heated. It is sparingly or not at all soluble in the ordinary solvents, readily soluble in boiling nitrobenzene.

Hexanitrodi-β-naphthylamine, $C_{20}H_9N(NO_2)_6$, prepared by heating the finely-powdered amine with fuming nitric acid, could not be obtained in crystals. It dissolves readily in alcohol, less in glacial acetic acid, and is almost insoluble in ether, benzene, cumene, and nitrobenzene. Alkaline carbonates dissolve it readily. When mixed with excess of copper oxide, it decomposes with explosive violence, and was therefore not analysed. The *potassium* and *barium* salts were analysed; they are both amorphous.

Benzoylorthonitrodi-β-naphthylamine, $C_{27}H_{16}NO \cdot NO_2$, is prepared by adding a mixture of fuming nitric and sulphuric acids to a solution of benzoyldi-β-naphthylamine in cold glacial acetic acid, and subsequently heating the whole at 50–60°. It crystallises from benzene in well-formed, yellow, transparent crystals (with 1 mol. C_6H_6), melting at 95°. Crystallised from alcohol it melts at 168°. It dissolves readily in warm benzene, less in alcohol.

Benzenyl naphthyleneamidine, $N \leq \begin{smallmatrix} CPh \\ C_{10}H_6 \end{smallmatrix} > N \cdot C_{10}H_7$, is obtained by reducing benzoylnitrodinaphthylamine dissolved in glacial acetic acid with excess of tin and hydrochloric acid. It crystallises from benzene in transparent, slender needles (with 1 mol. C_6H_6) melting at 113–114°; when crystallised from other solvents it melts at 163°. It sublimes when carefully heated in small, colourless plates, and distils

with slight decomposition. It is readily soluble. The *hydrochloride* forms slender, matted needles which decompose in contact with water.

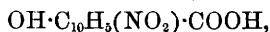
N. H. M.

Naphthaphenazine. By P. BRUNNER and O. N. WITT (*Ber.*, 20, 2660—2663). — *Naphthaphenazinesulphonic acid* is obtained when naphthaphenazine is heated with 10 times its weight of 35 per cent. fuming sulphuric acid at 100° for 12 hours. It crystallises in orange-red needles, melts above 290°, and is soluble in water and alcohol. In concentrated sulphuric acid it dissolves with a deep orange-brown colour, which becomes orange-yellow on dilution. The *sodium* salt, $C_{16}H_9N_2 \cdot SO_3Na + 2H_2O$, was prepared. On fusion with potassium hydroxide, a *eurhodol* is obtained which differs from that previously described (*Abstr.*, 1887, 153), since it dissolves in hydrochloric acid with a red colour, and in concentrated sulphuric acid with a dark-green colour changing to red on dilution. A similar compound has been prepared by diazotising the eurhodine formed by the reduction of nitronaphthaphenazine.

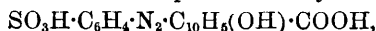
Cyanonaphthaphenazine, $C_{16}H_9N_2 \cdot CN$, is obtained when sodium naphthaphenazinesulphonate is distilled with potassium cyanide or dry potassium ferricyanide. Crystallised from cumene, it melts at 236—237°, and dissolves in concentrated sulphuric acid with a cherry-red colour, which changes through orange to yellow on dilution. If heated with hydrochloric acid under pressure, it is decomposed into naphthaphenazine and formic acid, but when heated with alcoholic potash at 220—230° it is partially converted into *naphthaphenazine-carboxylic acid*. This is sparingly soluble in the ordinary solvents, melts above 360°, and dissolves in concentrated sulphuric acid with a deep-red colour, changing to yellow on dilution. The *potassium* salt crystallises in white needles and is sparingly soluble in water.

W. P. W.

Naphtholcarboxylic Acids. By R. SCHMITT and E. BURKARD (*Ber.*, 20, 2699—2704). — α -*Naphtholcarboxylic acid* (m. p. 187°) can be prepared by heating sodium α -naphthol with liquid carbonic anhydride in an autoclave at 130°, and is a comparatively stable compound (compare *Abstr.*, 1887, 732), since it is only partially decomposed by prolonged boiling with water, in which it is very sparingly soluble. The aqueous solution is coloured greenish-blue by ferric chloride. The *sodium* salt, with 3 mols. H_2O , crystallises in large, thin, nacreous scales; the *ammonium* salt forms long needles; the *calcium* and *barium* salts crystallise in long needles. The *methyl* salt, $OH \cdot C_{10}H_7 \cdot COOMe$, melts at 78°, the *ethyl* salt at 49°, and the *phenyl* salt at 96°. The *acetyl*-derivative, $OAc \cdot C_{10}H_7 \cdot COOH$, melts at 158°; the *bromo*-derivative, $OH \cdot C_{10}H_7 \cdot Br \cdot COOH$, melts at 238°; the *nitro*-derivative,



melts at 202°, and yields β -nitro- α -naphthol when heated with lime; the *amido*-derivative melts above 200°, and its *acetyl*-compound at 185°. Metadiazonaphtholcarboxylic acid, $OH \cdot C_{10}H_7 \cdot \begin{smallmatrix} COO \\ N : N \end{smallmatrix}$, and parazobenzenesulphonic acid- α -naphtholcarboxylic acid,



were also obtained, and the latter on reduction with zinc and hydrochloric acid yields an amido- α -naphtholcarboxylic acid which crystallises in colourless, prismatic needles, is very sparingly soluble in water, and melts above 200° , but differs from the amido-derivative just described since its *acetyl*-compound melts at 195° .

When sodium β -naphthol is similarly heated with liquid carbonic anhydride in an autoclave at 130° , β -naphtholcarboxylic acid is obtained, and is separated by treating the product with ammonium carbonate and precipitating with hydrochloric acid. This acid readily decomposes on heating, and shows all the properties of Kauffmann's acid (Abstr., 1882, 1068). Ferric chloride colours its aqueous solution a pure blue. The ammonium salt crystallises in yellow needles, whilst the barium, calcium, and silver salts resemble the corresponding salts of the α -acid. The methyl salt melts at 76° , and the ethyl salt at 55° .

When sodium β -naphthol is heated at 280 – 290° in a current of carbonic anhydride, absorption of the gas rapidly takes place, and a product is obtained consisting of β -naphthol, undecomposed sodium β -naphthol, and β -naphtholcarboxylic acid. This acid is extremely stable, and crystallises from water in lustrous, rhombic, yellow scales, which melt at 216° without decomposition, and are readily soluble in alcohol and ether, soluble in toluene, benzene, and chloroform, and sparingly soluble in hot water. Ferric chloride colours the aqueous solution blue.

W. P. W.

Terpenes. Part VI. By O. WALLACH (*Annalen*, **241**, 315–328).—The compound which the author (Abstr., 1887, 967) recently described as terpene nitrite is *terpinene nitrosite*. It forms monoclinic crystals; $a : b : c = 1.0103 : 1 : 0.66978$; $\beta = 80^{\circ} 31'$.

Terpinene nitroethylamine, $\text{NHEt} \cdot \text{C}_{10}\text{H}_{15} : \text{NOH}$, is obtained by boiling for a short time an alcoholic solution of the nitrosite with a strong aqueous solution of ethylamine. The crude product is poured into water, the precipitate dissolved in hydrochloric acid, and the base reprecipitated by ammonia. The base melts at 130 – 131° , and dissolves in boiling alcohol, ether, chloroform, and in warm dilute solutions of alkalis. The *hydrochloride*, $\text{C}_{12}\text{H}_{22}\text{N}_2\text{O} \cdot \text{HCl}$, is crystalline, and dissolves freely in water and alcohol. The nitroso-compound melts at 132 – 133° . It is decomposed by boiling with an excess of hydrochloric acid, yielding hydroxylamine.

Terpinene nitroldiethylamine, $\text{NEt}_2 \cdot \text{C}_{10}\text{H}_{15} : \text{NOH}$, melts at 117 – 118° .

Terpinene nitrolmethylamine, $\text{NHMe} \cdot \text{C}_{10}\text{H}_{15} : \text{NOH}$, crystallises in prisms and melts at 141° . The *dimethylamine*, $\text{NMe}_2 \cdot \text{C}_{10}\text{H}_{15} : \text{NOH}$, melts at 160 – 161° . It dissolves in chloroform.

The *amylamine*-compound is less soluble in alcohol and ether than the preceding substances. It melts at 118 – 119° . The *piperidine*, $\text{C}_{10}\text{H}_{15}\text{NO} \cdot \text{NC}_5\text{H}_{10}$, melts at 153 – 154° . It is insoluble in alkalis, but its salts are freely soluble in water. The hydrochloride is obtained as an oil on passing dry hydrogen chloride into an ethereal solution of the base.

Terpinene nitrolamine is formed by adding ammonia to a hot

alcoholic solution of terpinene nitrosite. After recrystallisation from hot water it melts at 116—118°.

By adding a mixture of nitric acid and amyl nitrite to carvene or citronene saturated with dry hydrogen chloride, Maissen (*Gazzetta*, **13**, 99) obtained a crystalline compound melting with decomposition at 114—115°. The author has obtained the same or similar derivatives from cinnamene and dipentene. They melt at 109° and 110—111° respectively, and act on organic amines, yielding crystalline bases.

W. C. W.

Constitution of some Pyrroline-derivatives. By G. CIAMICIAN and P. SILBER (*Ber.*, **20**, 2594—2607; compare Abstr., 1887, 597).—*Dibromodiacetylpyrroline*, $C_4NHAc_2Pr_2$, is prepared by the action of bromine vapour on a warm solution of 2 grams of pyrrolenedimethyldiketone in 700 c.c. of water. It crystallises from alcohol in white needles melting at 171—172°, insoluble in water, soluble in alcohol, ether, and in alkaline carbonates. Nitric acid oxidises it readily at the ordinary temperature to dibromomaleimide; the constitution of the base is therefore $[Br_2 : Ac_2 = 3 : 4 : 2 : 5]$.

Nitrodibromacetylpyrroline, $C_4NHBr_2Ac \cdot NO_2$ $[Br_2 : Ac : NO_2 = 3 : 4 : 2 : 5]$, is formed when dibromodiacetylpyrroline (8 grams) is dissolved in fuming nitric acid (80 grams), and crystallises from alcohol in long, white needles melting at 206°. It is soluble in alcohol, ether, ethyl acetate, hot glacial acetic acid, and benzene, very sparingly soluble in water, insoluble in light petroleum. Alkaline carbonates dissolve it readily with intense yellow colour.

Dinitrodibromopyrroline, $C_4NHBr_2(NO_2)_2$ $[= 3 : 4 : 2 : 5]$, is obtained by the action of a well-cooled mixture of sulphuric and fuming nitric acids on the mononitro-compound. It crystallises from water in large, yellow plates (with 1 mol. H_2O), which melt at about 169° with decomposition; it is readily soluble in ether, alcohol, hot water, and hot benzene, and dissolves in alkaline carbonates with evolution of carbonic anhydride. If the mixed acids are allowed to act on the mononitro-compound at the ordinary temperature, dibromomaleamide, melting at 227°, is formed. The latter is also formed when dinitrodibromopyrroline is heated at 165°; nitric oxide is evolved.

When dinitrodibromopyrroline is heated with sulphuric acid (20 parts) it is converted quantitatively into dibromomaleic acid. It is probable that the imide of dibromomaleic acid, and, therefore, maleic acid also, are symmetrically rather than unsymmetrically constituted: $\llbracket \begin{smallmatrix} CBr \cdot CO \\ CBr \cdot CO \end{smallmatrix} \rrbracket NH$, rather than $\langle \begin{smallmatrix} CBr_2 \cdot CO \\ C \cdot CO \cdot NH \end{smallmatrix} \rangle$. (Compare Anschütz, Abstr., 1887, 916).

Dibromopyrrolinedicarboxylic acid behaves towards fuming nitric acid in a manner similar to dibromodiacetylpyrroline; dinitrodibromopyrroline $[NO_2 : NO_2 : Br : Br = 2 : 5 : 3 : 4]$ is formed identical with that obtained from dibromodiacetylpyrroline. The reaction shows that the two carboxyl-groups in pyrrolinedicarboxylic acid have the positions 2 : 5.

Methyl dibromopyrrolinedicarboxylate, $C_4NHBr_2(COOMe)_2$, is ob-

tained by dissolving methyl pyrrolinedicarboxylate (3 grams) in water (1 litre), and saturating the lukewarm solution with bromine vapour. The yield is 4.5 grams of pure product. It crystallises from alcohol in long, white needles, melting at 222° , soluble in ether, almost insoluble in water. When 2 grams of the salt is added to 40 grams of fuming nitric acid at -18° , and the whole poured into 400 c.c. of ice-water, and treated with potash (30 grams), the compound $C_4H_4BrNO_4$ is obtained. It is a crystalline compound, melting at $168-171^{\circ}$ with decomposition, soluble in ether, alcohol, and hot benzene, rather sparingly soluble in water, and insoluble in light petroleum. It dissolves in alkaline carbonates with evolution of carbonic anhydride. The constitutional formula $CBro\cdot C(NO_2)\cdot COOMe$ is suggested for it.

Methyl dibromacetylcarbopyrrolate, $C_4NHBr_2Ac\cdot COOMe$, is prepared in a manner similar to the methyl salt of the bromodicarboxylic acid, which it completely resembles in its behaviour towards fuming nitric acid.

Dibromacetylmethylpyrroline, $C_7H_7Br_2NO$, is prepared by treating a solution of 2 grams of acetylmethylpyrroline, melting at $85-86^{\circ}$ (Abstr., 1886, 719), with an excess of bromine. It crystallises from dilute alcohol in long, white needles, of a silky lustre, melts at $161-162^{\circ}$, dissolves in ether, carbon bisulphide, and chloroform, and is sparingly soluble in boiling water. When the finely-powdered compound is warmed with fuming nitric acid, dibromomaleimide (m. p. 227°) is formed. The constitution of acetylmethylpyrroline is therefore [$Ac : Me = 2 : 5$].

In order to obtain further evidence as to the constitution of pyruvyl methyl ketone and Schwanert's carbopyrrolic acid, tribromacetylpyrroline and methyl tribromocarbopyrrolate were converted into dibromomaleimide by the action of nitric acid.

Dibromonitracetylpyrroline, $C_4NHBr_2Ac\cdot NO_2$ [$Br : Br : Ac : NO_2 = 2 : 3 : 5 : 4$], is prepared by the action of bromine on nitracetylpyrroline, melting at 197° (Abstr., 1885, 810 and 992). It crystallises from alcohol in needles melting at 175° , soluble in ether, warm alcohol, and glacial acetic acid, sparingly soluble in warm water, insoluble in light petroleum. The non-identity of this compound with the dibromo-derivative described above, and the probability that in the nitracetyl-compound (m. p. 197°) the acetyl-group has the α -position, make it probable that the nitracetyl-compound has the constitution [$NO_2 : Ac = 3 \text{ or } 4 : 2 \text{ or } 5$].

A table of all pyrroline-derivatives (halogen-derivatives and ethers excepted) of known constitution is given. N. H. M.

Synthesis of Pyridine and Piperidine-derivatives. By C. PAAL and C. STRASSER (*Ber.*, 20, 2756—2766).—Diphenacylacetic acid (Abstr., 1887, 261) when treated with alcoholic ammonia yields the ammonium salt of $\alpha\alpha'$ -diphenyldihydropyridine- γ -carboxylic acid, $C_6NH_4Ph_2\cdot COONH_4$. This salt is soluble in water and concentrated hydrochloric acid; on acidification with sulphuric acid, the corresponding acid separates, but is quickly decomposed. On dry distillation, ammonia is given off, and $\alpha\alpha'$ -diphenylpyridinecarboxylic acid,

$C_5NH_2Ph_2 \cdot COOH$, is produced, which after purification crystallises in delicate, white needles or prisms, melting at 275° , soluble in alcohol, sparingly soluble in chloroform. The acid is not altered by nitrous acid, acetic chloride, or oxidising agents. Its ammonium salt does not exist in the free state; the *silver* salt is a heavy, white precipitate; the *chromate* a dark-red, amorphous precipitate; the *aurochloride* is crystalline.

$\alpha\alpha$ -Diphenylpiperidine- γ -carboxylic acid, $C_5NH_3Ph_2 \cdot COOH$, obtained together with the above acid, and separated from it by its greater solubility, forms crystalline crusts; it melts at 339° , and sublimes without decomposition, its alkaline salts are very soluble, the *barium* and *silver* salts are white precipitates. Its *nitroso-derivative* crystallises in pale-yellow, glistening needles melting at 159° , and is soluble in ether and alcohol.

$\alpha\alpha$ -Diphenylpyridine, C_5NH_3Ph , obtained by the distillation of the calcium salt of the carboxylic acid with lime, crystallises in long, glistening needles melting at $81-82^\circ$; its *platinochloride* forms yellow needles, and the *aurochloride* a crystalline precipitate; the *methiodide* crystallises in needles melting at 203° .

$\alpha\alpha$ -Diphenylpiperidine, $C_5NH_3Ph_2$, obtained by the hydrogenation of the above base, is a thick, pale-yellow oil; its *hydrochloride* crystallises in white needles; the *platinochloride* and the *aurochloride* and the *nitroso-derivative* crystallise with difficulty. V. H. V.

3-Methylpyridine and 3-Methylpiperidine. By C. STOEHR (*Ber.*, 20, 2727—2733).—The picoline obtained by distilling strychnine with lime (*Abstr.*, 1887, 604) proves on further examination to be β -picoline, since nicotinic acid is found to be the sole product on oxidation with 2 per cent. permanganate solution. Some quantity of the base was prepared to enable an examination of its properties to be made, and the results are compared with those of previous observers. β -Picoline thus obtained boils at $145-150^\circ$ after two fractionations; by conversion of this product into the mercurochloride and regeneration of the base, it gives a product which mostly passes over between 148° and 149° (compare Hesekei, *Abstr.*, 1885, 812). The *platinochloride*, $(C_6H_7N)_2, H_2PtCl_6 + H_2O$, has the properties of the salt described by Baeyer (*Annalen*, 155, 285), melts when dry at 195° , loses 1 mol. H_2O when allowed to remain in a desiccator, and when heated at 120° loses in addition 1 mol. HCl , the compound thus obtained, $(C_6H_7N)_2, HCl, PtCl_4$, melting at $211-212^\circ$. The *aurochloride* melts at $182-183^\circ$. The *mercurochloride*, $C_6H_7N, HCl, 2HgCl_2$ (compare Hesekei, *Abstr.*, 1886, 256), crystallises from hot water in slender, ramifying needles, from dilute hydrochloric acid in indented scales, or long, compact needles, and from concentrated hydrochloric acid, in which it is very soluble, in small, well-formed prismatic crystals melting at $139-140^\circ$. The *picrate* crystallises in six-sided scales melting at $142-143^\circ$.

3-Methylpiperidine, obtained by reduction of the β -picoline in alcoholic solution with sodium, is readily soluble in water, and yields a *hydrochloride*, crystallising in dazzling, white needles.

W. P. W.

2 : 6 Methylethylpyridine and 2 : 4 Methylethylpyridine.

By M. SCHULTZ (*Ber.*, **20**, 2720—2727).—Picoline ethiodide, when heated at 280—300° for 1 to 1½ hours, yields a mixture of bases. To separate these, the product is treated with water, acidified, distilled to remove a small quantity of an aromatic oil, then rendered alkaline and again distilled. The mixture of bases so obtained, which boils between 100° and 200°, is fractionated, and the fractions boiling at 156—166°, 166—172°, and 172—182° repeatedly refractionated; in this way fractions boiling at 158—163° and 169—174° are obtained, and these consist chiefly of 2 : 6 methylethylpyridine and 2 : 4 methylethylpyridine respectively.

2 : 6 *Methylethylpyridine*, $C_8H_{11}N$, is a colourless, hygroscopic, oily liquid, having a sweet, aromatic odour recalling that of picoline, and when moist, an alkaline reaction. It is sparingly soluble in water, readily volatile with steam, and yields salts which readily deliquesce in air. The *platinochloride*, $(C_8H_{11}N)_2 \cdot H_2PtCl_6$, crystallises in tabular, triclinic crystals, melts at 173—174° (after drying at 110°), and is readily soluble in hot water, insoluble in alcohol and ether; the *aurochloride*, $C_8H_{11}N \cdot HAuCl_4$, crystallises in yellow needles, melts at 110°, and is sparingly soluble in water, readily soluble in ether alcohol. On reduction with sodium in hot alcoholic solution, *copellidine*, $C_8H_{17}N$ [Me : Et = 2 : 6], is obtained; this is a colourless, oily liquid, which boils at 147—151°, fumes slightly in the air, has the characteristic odour of piperidine bases, and a strongly alkaline reaction. The *nitroso-derivative* is a brown oil; the *hydrochloride*, $C_8H_{17}N \cdot HCl$, crystallises in white needles, and though readily soluble in water and alcohol is only slightly hygroscopic. When oxidised with 2 per cent. permanganate solution, 2 : 6 methylethylpyridine is converted into a dicarboxylic acid melting at 226°, and identical with Ladenburg and Roth's dipicolinic acid (*Abstr.*, 1885, 557).

2 : 4 *Methylethylpyridine*, [Me : Et = 2 : 4], is a hygroscopic, colourless, oily liquid, which in its properties closely resembles the 2 : 6-derivative. The *platinochloride*, $(C_8H_{11}N)_2 \cdot H_2PtCl_6$, forms reddish-yellow, tabular crystals, which after drying at 110° melt at 190°; the *aurochloride*, $C_8H_{11}N \cdot HAuCl_4$, crystallises in yellow needles, begins to fuse at 83°, melts at 90°, and is soluble in hot water, readily soluble in alcohol and ether. When the base is reduced with sodium in hot alcoholic solution, it is converted into *copellidine*, [Me : Et = 2 : 4] $C_8H_{17}N$; this is a colourless, oily liquid, which boils at 155—160°, has a strongly alkaline reaction, and an odour similar to that of the 2 : 6 base. The *hydrochloride*, $C_8H_{17}N \cdot HCl$, crystallises in white needles, is readily soluble in water and alcohol, and is slightly hygroscopic. On oxidation with 2 per cent. permanganate solution in the cold or on heating, 2 : 4 methylethylpyridine yields a dicarboxylic acid whose melting point rose from 204° to 211° after three crystallisations. This author regards this acid as being identical with Ladenburg and Roth's lutidinic acid (*Abstr.*, 1885, 815), and ascribes its lower melting point to the presence of a small quantity of picolinic acid.

W. P. W.

Phenylated Piperidine and Pyridine Bases. By O. BALLY (*Ber.*, **20**, 2590—2594).—*γ-Phenylpiperidine*, $C_8H_{10}Ph$, is prepared from *γ*-phenylpyridine and purified by distillation. It melts at $57.5-58^\circ$, and boils at $255-257^\circ$ under 727 mm. pressure; it is a strong base, almost insoluble in water. The salts are readily soluble. The *hydrochloride* crystallises in needles; the *platinochloride* forms orange-coloured plates, melting at $204-207^\circ$. It gives no precipitate with picric acid; the original base gives a precipitate even in very dilute solution.

Phenyllutidine, $C_8NH_2Me_2Ph$ [$Me : Ph : Me = 2 : 4 : 6$], is obtained by distilling potassium phenyllutidinecarboxylate (prepared from benzaldehyde, ethyl acetoacetate, and ammonia) with lime, at the lowest possible temperature. It is purified by means of the *hydrochloride*, and crystallises from ether in prisms melting at $54.5-55^\circ$. It boils at 287° under 731 mm. pressure. The salts are generally sparingly soluble; the *hydrochloride* (with 3 mols. H_2O) crystallises in slender, matted needles which do not melt at 300° ; the *platinochloride*, $(C_{13}H_{13}N)_2, H_2PtCl_2 + 4H_2O$, forms orange-coloured needles; the *nitrate* and *chromate* melt at 177° and 222° respectively, both crystallise in needles.

γ-Phenyllupetidine, $C_8NH_8PhMe_2$, is prepared by the action of sodium (2.5 parts) on phenyllutidine (1 part) dissolved in absolute alcohol; it is separated from unchanged phenyllutidine by distillation. It is a colourless oil of a peculiar odour, boiling at 274° under 731 mm. pressure. The *hydrochloride* and *nitrate* crystallise in prisms; the *dinitrate* melts at 210° ; the *platinochloride* crystallises in gold-coloured plates melting at 237° . Besides phenyllupetidine, a compound, probably *heptylbenzene*, $CHPh(CH_2 \cdot CH_2Me)_2$, is produced in the reduction of phenyllutidine.

When *γ-phenyllutidylum methiodide* (prepared by digesting the base with methyl iodide in a reflux apparatus) is treated with strong aqueous potash, a base is obtained which yields a hydrochloride identical with that formed by the action of silver chloride on methylphenyllutidylum iodide.

Methyl-*γ-phenyllutidylum iodide* is a crystalline substance sparingly soluble in hot water. N. H. M.

***α*-Cinnamylpyridine.** By H. BAURATH (*Ber.*, **20**, 2719—2720).—When *α*-picoline and benzaldehyde in equimolecular proportions are heated with zinc chloride at $220-225^\circ$ for six hours, *α-cinnamylpyridine*, $C_8NH_4 \cdot CH : CHPh$, is obtained, and after removal of unaltered benzaldehyde by steam distillation can be separated by rendering the product alkaline and distilling with superheated steam. The base, already prepared but not described by Jacobsen and Reimer (*Abstr.*, 1884, 335), is crystalline, melts at $90.5-91^\circ$, boils at $313-314^\circ$ (uncorr., under 753 mm. pressure), and is readily soluble in carbon bisulphide and ether, soluble in alcohol, benzene, and light petroleum, and practically insoluble in water. The salts generally crystallise in needles: the *platinochloride*, $(C_{13}H_{11}N)_2, H_2PtCl_6 + 2H_2O$, decomposes when heated to expel the water of crystallisation. On treatment with bromine in carbon bisulphide solution, the base yields

an additive compound, $C_{13}H_{11}NBr_2$, which crystallises from alcohol in compact needles melting at $166-167^\circ$; this derivative yields a new base when heated with alcoholic potash. Derivatives of α -cinnamylpyridine have also been obtained by the action of hydriodic acid and by reduction of sodium and alcohol, and will be described in a later communication.

W. P. W.

Ethylquinoline. By L. REHER (*Ber.*, **20**, 2734—2735).—Doebner having found the boiling point of α -ethylquinoline to be $245-246^\circ$ (Abstr., 1887, 504), the author has redetermined the boiling points of α - and γ -ethylquinoline (*ibid.*, 279) by converting the bases into the platinochlorides, recrystallising these repeatedly from concentrated hydrochloric acid, and regenerating the bases from the pure salts by means of hydrogen sulphide. α -Ethylquinoline boils at $256.6-258.6^\circ$ (corr.) and γ -ethylquinoline boils at $271-274^\circ$ (corr.), and the pure platinochlorides melt at 189° and 203° respectively. From the pure bases, *chromates* were prepared crystallising in red needles, and crystalline *zincchlorides* were also obtained, that of the γ -base forming white, concentrically-grouped needles melting at 195° .

Diethylquinoline, obtained by the decomposition of the mercuriochloride (*loc. cit.*), is a colourless liquid having a quinoline-like odour, and boiling at $282.8-284.8^\circ$ (corr.). The *platinochloride*, $(C_9H_5NEt_2)_2, H_2PtCl_6$, crystallises in orange-red needles, and melts at 217° after previous blackening. On oxidation with chromic acid, the base yields a small quantity of an acid which crystallises in asbestos-coloured needles melting at 190° .

W. P. W.

Orthohydroxyquinolinecarboxylic Acid. By R. SCHMITT and F. ENGELMANN (*Ber.*, **20**, 2690—2695).—Further examination of orthohydroxyquinolinecarboxylic acid (Abstr., 1887, 738) shows that it begins to fuse at 137° , that carbonic anhydride and orthohydroxyquinoline are formed at $144-145^\circ$, and that the decomposition is complete at 150° . The *ammonium* salt, $OH \cdot C_9NH_5 \cdot COONH_4 + H_2O$, crystallises in glistening, pale-yellow needles, and is soluble in water; the *barium* salt, $(OH \cdot C_9NH_5 \cdot COO)_2Ba + 2H_2O$, crystallises in long, silky needles, and is sparingly soluble in water; the *calcium* salt crystallises in stellate groups of prisms; a basic barium salt, $C_{10}NH_5O_3Ba$, and a basic calcium salt were also prepared; the former is very sparingly soluble in water. The *phenyl* salt, $OH \cdot C_9NH_5 \cdot COOPh$, obtained by heating equimolecular proportions of the acid and phenol at 170° , forms colourless, short prisms and melts at $225-226^\circ$. The *hydrochloride* of the acid, $OH \cdot C_9NH_5 \cdot COOH, HCl$, crystallises in large prisms, and the *nitrate* in yellow needles; both salts are decomposed by water. On treatment with strong nitric acid, a dinitrohydroxyquinoline is obtained which is probably identical with that described by Bedall and Fischer (Abstr., 1881, 613; *Ber.*, **14**, 1368); it crystallises in golden-yellow scales, melts at 276° with blackening and the evolution of gas, is sparingly soluble in most solvents, and readily decomposes alkaline carbonates, forming the corresponding salts.

Nitrohydroxyquinolinecarboxylic acid, $NO_2 \cdot C_9NH_4(OH) \cdot COOH$, is prepared by heating the nitrate of orthohydroxyquinolinecarboxylic

acid with acetic acid at 100° ; the resulting brown mass is extracted with acetic acid until it becomes yellow, and is then purified by solution in hydrochloric acid and subsequent precipitation with water. It crystallises from water in yellow needles showing a vitreous lustre, decomposes at 200° with the evolution of carbonic anhydride, and dissolves readily in concentrated hydrochloric acid, in alkalis and in alkaline carbonates, but is sparingly soluble in acetic acid. When heated above 200° , *nitrohydroxyquinoline*, $\text{NO}_2 \cdot \text{C}_9\text{NH}_5 \cdot \text{OH}$, is formed; this crystallises in yellow needles, melts at 173° , is readily soluble in acetic acid and hot hydrochloric acid, less so in alcohol and ether. On treatment with bromine (2 mols.) at 100° , a dibromohydroxyquinoline identical with that prepared by Bedall and Fischer (*loc. cit.*) is obtained together with *bromohydroxyquinolinecarboxylic acid*, $\text{OH} \cdot \text{C}_9\text{NH}_5 \cdot \text{Br} \cdot \text{COOH}$; this crystallises in matted, citron-yellow needles, melts at $233-235^{\circ}$ with the evolution of carbonic anhydride, and yields a hydrochloride which crystallises in well-formed tables, and decomposes when boiled with water. *Bromohydroxyquinoline*, $\text{C}_9\text{NH}_5 \cdot \text{Br} \cdot \text{OH}$, formed quantitatively when the bromo-acid is heated at 200° , crystallises in white needles, melts at $119-120^{\circ}$, and is readily soluble in the ordinary solvents except water. W. P. W.

Parahydroxyquinolinecarboxylic Acid. By R. SCHMITT and J. ALTSCHUL (*Ber.*, **20**, 2695—2698).—When potassium parahydroxyquinoline is heated with liquid carbonic anhydride in an autoclave at 170° for six to seven hours, a quantitative yield of potassium parahydroxyquinolinecarboxylate is obtained; the sodium-compound cannot be substituted for the potassium-derivative in this reaction. *Parahydroxyquinolinecarboxylic acid*, $\text{OH} \cdot \text{C}_9\text{NH}_5 \cdot \text{COOH}$, crystallises from water in yellowish-white flocks consisting of microscopic prisms, melts at $203-204^{\circ}$ with the evolution of carbonic anhydride and formation of parahydroxyquinoline, and is sparingly soluble in alcohol, ether, benzene, and hot water. Ferric chloride colours the aqueous solution red. The *hydrochloride*, $\text{OH} \cdot \text{C}_9\text{NH}_5 \cdot \text{COOH} \cdot \text{HCl}$, crystallises in long, colourless needles, or from concentrated hydrochloric acid in short, thick prisms, is decomposed by water, and yields a well-crystallised platinochloride; the *nitrate*, formed by digesting the acid with nitric acid (sp. gr. = 1.35), crystallises in large, white needles, and is decomposed by water. The *ammonium salt*, with $\frac{1}{2}$ mol. H_2O , crystallises in long, colourless needles, and is soluble in water, the solution evolving ammonia when boiled; the *barium salt*, with 2 mols. H_2O , crystallises in colourless tufts of needles, and does not form a basic salt when treated with barium hydroxide.

If the nitrate of parahydroxyquinolinecarboxylic acid is heated with nitric acid, yellowish-red prisms separate on cooling, which when treated with water decompose into nitric acid and nitrohydroxyquinoline; this crystallises in yellow needles, melts at 136° , and is probably identical with Skrap's nitrohydroxyquinoline (*Abstr.*, 1882, 92).

W. P. W.

Constitution of Glutazine. By H. v. PECHMANN (*Ber.*, **20**, 2655—2658; compare *Abstr.*, 1887, 155).—*Nitroglutazine*, $\text{C}_5\text{H}_5\text{N}_2\text{O}_2 \cdot \text{NO}_2$,
f 2

is obtained together with dinitroglutazine when nitrous oxide is passed into a cold aqueous solution of glutazine. It crystallises from water in orange-yellow plates which decompose at $170-180^{\circ}$ without melting. *Dinitroglutazine*, $C_5H_4N_2O_2(NO_2)_2$, crystallises from water in yellow plates. Both compounds give colourless solutions with acetic acid and zinc-dust which become red when exposed to air. When heated with alkali, they are converted, with evolution of ammonia, into sparingly soluble salts which crystallise in sulphur-coloured, matted needles and explode when heated. These results make it improbable that glutazine contains an amido-group.

The *nitronitrosamine*, $NO_2C_5H_4N_2O_2NO$, is obtained when glutazine (1 part) dissolved in the smallest amount of dilute aqueous soda is treated with sodium nitrite (1 part); water is added (so that the whole amounts to 30 parts), and the whole is poured into a mixture of glacial acetic acid (5 parts) and water (30 parts). In a short time it solidifies to an orange-coloured magma. The *sodium salt*, $C_5H_3NaN_4O_5$, so obtained crystallises in yellow needles with water of crystallisation. Acids precipitate greenish-yellow needles from the solution. When the sodium salt dissolved in glacial acetic acid is warmed with excess of sodium nitrite, the *sodium salt* of the *dinitronitrosamine*, $C_5H_2NaN_5O_7$, separates as a cinnabar-coloured, crystalline powder. This dissolves sparingly in water, readily in alkalis. When warmed with dilute acids nitrous acid is given off.

Dibenzoylglutazine, $C_5H_4N_2O_2Bz_2$, is obtained by heating glutazine with benzoic chloride on a water-bath for two to three hours, and crystallises from glacial acetic acid in lustrous, brownish plates melting at $215-216^{\circ}$. It is insoluble in water and in alkalis, sparingly soluble in alcohol.

The above results show that there are only two hydrogen-atoms in glutazine displaceable by acid radicles, and that these are present as imido-hydrogen as shown by the formula $NH < \begin{smallmatrix} CO \cdot CH_2 \\ CO \cdot CH_2 \end{smallmatrix} > C : NH$.

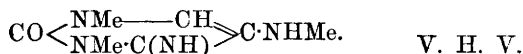
N. H. M.

Reactions of Caffeine and Caffèidine. By M. WERNECKE (*Chem. Centr.*, 1887, 1082—1084).—Hydriodic acid, like hydrochloric acid, decomposes caffeine into carbonic oxide and anhydride, formic acid, sarcosine, ammonia, and methylamine; if phosphorus is added, glycocine is formed instead of sarcosine, whilst hydrogen phosphide and phosphonium iodide are evolved. Although methyl iodide readily combines with caffeine to form the methiodide, the formation of the corresponding ethyl-compound presents considerable difficulty. Phenylhydrazine will not combine with caffeine; from this it would seem that in this case, as an analogue of carbamide, the carbonyl-group is directly combined with the nitrogen-atom.

Caffeine chloriodide, $C_8H_{10}N_4O_2, HI$, is produced when sodium nitrite and potassium iodide are added to a hydrochloric acid solution of this base; it forms golden needles melting at $182-183^{\circ}$, and is decomposed into its constituents by ammonia or by boiling with water. The method proposed by Maly and Andreasch for the preparation of caffeine presents no advantage over that of Strecker. Caffeine sulphate

differs from the hydroiodide in that the former, when heated, turns purple-red, whilst the latter yields a green mass; the anurochloride of caffeine cannot be isolated. The base is best separated from the sulphate by means of basic lead carbonate. *Methylcaffeidine hydroiodide* is not a well-defined substance, but the free base is crystalline and melts at 86–88°; *dimethylcaffeidine* forms leaflets melting at 123°.

The author ascribes the following constitution to caffeidine,



Hydroquinine. By O. HESSE (*Annalen*, **241**, 255–287).—*Hydroquinine*, $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2$, exists ready formed in cinchona bark, and is present in varying quantities in commercial quinine. It is conveniently prepared from the mother-liquor obtained in the manufacture of the acid sulphate of quinine. The mother-liquor is neutralised and the neutral salt dissolved in sulphuric acid, quinine monosulphate crystallises, and the mother-liquor containing the hydroquinine is again neutralised. By repeating these operations a salt is obtained containing 30 per cent. of hydroquinine sulphate. The quinine is removed by oxidising the solution in sulphuric acid with potassium permanganate, the mixture is filtered and the hydroquinine liberated by the addition of an alkali and extracted with ether. The base is deposited from its solution in chloroform in needles and from hot acetone in long plates. Many of the properties of the compound have been previously described by the author (*Abstr.*, 1882, 1113). It is lævogyrate $[\alpha]_D = -142.2^\circ$ for a 2.4 per cent. solution in 95 per cent. alcohol at 20°, and $[\alpha]_D = -227.1^\circ$ for an aqueous solution of the same strength under similar conditions. (40 c.c. normal hydrochloric acid were contained in each 100 c.c. of water used for the solution.) When ammonia is added to a solution of equal molecular proportions of cupreine and hydroquinine in water containing sulphuric acid, and the acid mixture extracted with ether, a crystalline compound of cupreine and hydroquinine is obtained, $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2 \cdot \text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2 + 2\text{H}_2\text{O}$. Hydroquinine forms similar compounds with conchinine and hydroconchinine. It also unites with two and with three molecules of cinchonidine, forming crystalline compounds which do not contain any water of crystallisation. Analogous compounds are formed with hydrocinchonidine and with homocinchonidine.

Anethoilhydroquinine, $(\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2)_2 \cdot \text{C}_{10}\text{H}_{12}\text{O} + 2\text{H}_2\text{O}$, is deposited in quadratic prisms from a solution of 5 parts of hydroquinine and 1 part of anethoil in warm alcohol.

Hydroquinine forms three series of salts, which are as a rule more soluble than the corresponding salts of quinine. The normal sulphate, $(\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2)_2 \cdot \text{H}_2\text{SO}_4 + 6\text{H}_2\text{O}$, has been previously described (*loc. cit.*). It forms a crystalline compound with phenol, $(\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2)_2 \cdot \text{SO}_3 \cdot \text{C}_6\text{H}_6\text{O} + 2\text{H}_2\text{O}$, which is sparingly soluble in cold water. The acid sulphate, $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2 \cdot \text{SO}_4\text{H}_2 + 3\text{H}_2\text{O}$, is freely soluble in water and alcohol. At 140°, the anhydrous salt is converted into hydroquinine sulphate. The disulphate is amorphous. Dichroic crystals resembling hydro-

quinine herepathite are obtained by adding potassium iodide (2 mols.) to an alcoholic solution of the acid sulphate (4 mols.), and acting on the product with an alcoholic solution of iodine.

Hydroquinine hyposulphite, $(C_{20}H_{26}N_2O_2)_2 \cdot H_2S_2O_3 + 2H_2O$, forms white prisms sparingly soluble in water. The *hydrochloride*,



crystallises in prisms, and is freely soluble in alcohol and water. The *platinochlorides*, $(C_{20}H_{26}N_2O_2)_2 \cdot H_2PtCl_6 + 3H_2O$ and $C_{20}H_{26}N_2O_2 \cdot H_2PtCl_6 + 2H_2O$, are amorphous and are sparingly soluble in water; the *mercurochloride*, $(C_{20}H_{26}N_2O_2 \cdot HCl)_2 \cdot HgCl_2$, crystallises in needles. The *hydrobromides*, $C_{20}H_{26}N_2O_2 \cdot HBr + 2H_2O$ and $C_{20}H_{26}N_2O_2 \cdot 2HBr + 3H_2O$, also form needles. The neutral *hydriodide* is a colourless oily liquid which solidifies to an amorphous mass. Potassium iodide produces in acid solutions of hydroquinine salts a yellow, crystalline precipitate of the acid hydriodide, $C_{20}H_{26}N_2O_2 \cdot 2HI + 4H_2O$. On the addition of iodine to the alcoholic solution of this salt, dichroic, needle-shaped crystals of the composition $C_{20}H_{26}N_2O_2 \cdot 2(IH, I_2)$ are deposited. The *acetate*, $C_{20}H_{26}N_2O_2 \cdot C_2H_3O_2 + 5H_2O$, crystallises in needles and is freely soluble in alcohol and water. The *benzoate* and *salicylate* dissolve freely in alcohol. The benzoate is anhydrous. The *piperonate*, $C_{20}H_{26}N_2O_2 \cdot C_8H_5O_4$, is soluble in water and in chloroform. The *oxalate* is deposited from hot alcohol in prisms containing 6 mols. H_2O . The *tartrate* also crystallises in prisms containing 2 mols. H_2O . It is soluble in alcohol, water, and in a mixture of alcohol and chloroform. The *citrate* and *arsenate* crystallise with 10 mols. H_2O , the *phosphate* with 7 mols. H_2O . The *chromate*, $(C_{20}H_{26}N_2O_2)_2 \cdot H_2CrO_4 + 6H_2O$, forms golden needles. The *dichromate* is an oily liquid.

Hydroquinicine dissolves freely in ether, alcohol, chloroform, and in dilute acids. The solution in dilute sulphuric acid is yellow; the colour changes to green on the addition of chlorine water and ammonia, but the mixture is not fluorescent. An ethereal solution of oxalic acid produces in an ethereal solution of hydroquinicine an amorphous precipitate soluble in chloroform. The normal sulphate crystallises in needles and dissolves freely in alcohol and in water.

Hydroquinine platinochloride, $C_{20}H_{26}N_2O_2 \cdot H_2PtCl_6 + H_2O$, forms orange-coloured crystals. Hydroquinine unites with methyl iodide, forming the compound $C_{20}H_{26}N_2O_2 \cdot MeI + C_2H_5O$. It crystallises in prisms of a yellow colour and dissolves in hot alcohol. It melts at 218° . On treatment with silver chloride, it is converted into the chloride $C_{20}H_{26}N_2O_2 \cdot MeCl + 2H_2O$. The acid *platinochloride*, $C_{20}H_{26}N_2O_2 \cdot Me \cdot HPtCl_6 + 2H_2O$, forms orange-coloured crystals, and the normal salt, $(C_{20}H_{26}N_2O_2 \cdot Me)_2 \cdot PtCl_6$, pale-yellow needles. *Hydroquinine methylhydroxide* is amorphous. It is soluble in alcohol and water. The solutions are caustic and absorb carbonic anhydride.

Acetylhydroquinine, $C_{20}H_{26}N_2O_2 \cdot Ac$, is amorphous. It melts at 40° and dissolves freely in alcohol, ether, benzene, and in acids. The solution is lævogyrate, and the solution in sulphuric acid is fluorescent. The *platinochloride* contains 2 mols. H_2O , and the normal sulphate,

which is soluble in hot water and alcohol, crystallises with 9 mols. H_2O .

Hydroquinine is converted into hydrocupreine dihydrochloride by the action of hydrochloric acid, sp. gr. 1.125, at 150° . *Hydrocupreine*, $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_2 + 2\text{H}_2\text{O}$, exists as a crystalline powder freely soluble in ether, alcohol, and chloroform. It melts at 168 – 170° , and exhibits a strong basic reaction and forms crystalline salts. Solutions of the normal salts have a greenish-yellow colour, the acid salts are colourless. The *sulphate*, $(\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_2)_2 \cdot \text{H}_2\text{SO}_4$, is sparingly soluble in water and in alcohol. The *tartrate* is sparingly soluble in water, but the dihydrochloride, $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_2 \cdot 2\text{HCl} + \text{H}_2\text{O}$, is freely soluble in water. The acid platinumchloride, $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_2 \cdot \text{H}_2\text{PtCl}_6$, is crystalline and insoluble in water.

Hydroquininesulphonic acid, $\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_2 \cdot \text{SO}_3\text{H} + \text{H}_2\text{O}$, is prepared by dissolving hydroquinine in sulphuric acid at the ordinary temperature. The solution is poured into water and mixed with excess of ammonia. The acid crystallises in cubes and is soluble in boiling water, alcohol, and hot solutions of alkalis. It dissolves freely in acids, with which it forms crystalline compounds. The anhydrous acid melts at 239° .

The presence of hydroquinine in cinchona bark vitiates the results obtained in the estimation of quinine by the ordinary polariscopic method.

W. C. W.

Apocinchine and Apochinine. By W. J. COMSTOCK and W. KOENIGS (*Ber.*, 20, 2674–2689).—Analyses of salts and bromo-derivatives of apocinchine show that the formula previously assigned to the base (*Abstr.*, 1882, 224) must be altered to $\text{C}_{19}\text{H}_{19}\text{NO}$; the formula ascribed to ethylapocinchinic acid (*Abstr.*, 1885, 1248) is, however, retained. The authors now attribute the formation of the combustible, gaseous halogen compound (? methyl chloride) in the preparation of apocinchine to some secondary change in the reaction. *Apocinchine hydrobromide*, $\text{C}_{19}\text{H}_{19}\text{NO} \cdot \text{HBr}$, crystallises from alcoholic hydrogen bromide in small, yellow needles, and melts at about 256° ; the *hydriodide*, $\text{C}_{19}\text{H}_{19}\text{NO} \cdot \text{HI}$, is a yellow, crystalline salt; the *platinchloride*, $(\text{C}_{19}\text{H}_{19}\text{NO})_2 \cdot \text{H}_2\text{PtCl}_6$, forms orange-yellow crystals and melts at about 235° . The *acetyl*-derivative, $\text{C}_{19}\text{H}_{18}\text{NOAc}$, forms practically colourless crystals, and melts at 118 – 119° ; the double phosphates of apocinchine and ammonium, barium, and potassium, were also prepared, and crystallise well.

Bromapocinchine, $\text{C}_{19}\text{H}_{18}\text{NOBr}$, is prepared by gradually adding bromine to apocinchine hydrobromide dissolved in equal parts of chloroform and acetic acid until the yellow perbromide begins to separate; sodium hydrogen sulphite is then added and the base obtained from the chloroform and aqueous layers by evaporation and precipitation. It is crystalline, melts at 186 – 188° , and is readily soluble in aqueous soda, benzene, chloroform, and ethyl acetate, less so in alcohol, carbon bisulphide, ether, and light petroleum. Bromapocinchine is not altered by prolonged boiling with alcoholic soda, and yields bromoform and cinchonic acid on oxidation with 4 per cent. chromic acid solution.

Dibromethylapocinchine, $C_{19}H_{16}NBr_2 \cdot OEt$, is prepared by adding ethylapocinchine (10 grams) to well-cooled bromine (15 c.c.), digesting the product after 12 hours with sodium hydrogen sulphite, and extracting with alcoholic ammonia; the deposit from the alcoholic solution is then boiled with dilute sulphuric acid, the resulting solution treated with ether and aqueous soda, and the base obtained from the ethereal layer by evaporation. It melts at 116—118°. The alkaline solution, after separation from the ether, is found to contain dibromapocinchine.

Ethylapocinchinic acid forms a crystalline hydrochloride and hydrobromide. The *silver* salt, $C_{20}H_{18}NO_3Ag$, is a white, crystalline salt unaffected by light; the *platinochloride*, $(C_{20}H_{18}NO_3)_2 \cdot H_2PtCl_6$, is precipitated in voluminous, slender, straw-yellow needles, which are converted into small, compact, orange-yellow crystals, when the salt is heated on a water-bath for a short time.

Homapocinchine, $C_{17}H_{15}NO$, the compound formed together with carbonic anhydride and ethyl chloride when ethylapocinchinic acid is heated at 130° with hydrochloric acid (*loc. cit.*), crystallises from dilute alcohol in colourless crystals which contain water of crystallisation and melt at 184—185°. It is sparingly soluble in water, ether, benzene, and chloroform, readily soluble in hot alcohol, and differs from apocinchine, to which it shows much similarity, in its ready solubility in dilute aqueous soda. The *hydrobromide*, $C_{17}H_{15}NO_3 \cdot HBr + H_2O$, crystallises in glistening, transparent, yellow needles or prisms, melts at 221—222°, and is sparingly soluble in water and in excess of dilute hydrobromic acid. The *ethyl-derivative* yields a crystalline, yellow sulphate. On fusion with potassium hydroxide, homapocinchine is converted into a compound which probably corresponds to oxyapocinchine. When oxidised in very dilute solution with permanganate, ethylapocinchine yields a mixture of solid acids which dissolve in dilute sulphuric acid and alkalis. Ethylapocinchinic acid is one constituent of the mixture. To effect a separation, the product is boiled with hydrobromic acid (sp. gr. 1.49), and the solution treated with aqueous soda which precipitates homapocinchine; careful acidification of the filtrate then precipitates a mixture of at least two acids, of which the one of lower melting point is the more soluble in alcohol. The more soluble acid, $C_{18}H_{13}NO_4$ or $C_{19}H_{15}NO_4$, dissolves in dilute mineral acids, melts at 230° with the evolution of gas, and at 240° yields carbonic anhydride and a compound, $C_{17}H_{13}NO_2$. This crystallises from dilute alcohol in colourless, silky needles, melts at 223°, is not volatile without decomposition, and is soluble in dilute acids and alkalis. The hydrobromide, sulphate, and nitrate are crystalline, and sparingly soluble.

Acetyloxyapocinchine, $C_{19}H_{16}NO_2Ac$, melts at 201—203°, and is soluble in alcohol, benzene, and light petroleum.

From considerations based on analyses of its salts, the authors have adopted the formula $C_{19}H_{15}NO_2$ for chinine, instead of that previously proposed (Abstr., 1885, 910). *Chinine hydrobromide*, $C_{19}H_{15}NO_2 \cdot HBr$, crystallises in long, sulphur-yellow needles, and is decomposed by water.

The remainder of the paper is devoted to a discussion of the con-

stitution of these alkaloids, in which the authors adhere to the views already put forward with regard to apocinchine (Abstr., 1885, 1248; 1887, 600), and suggest that cinchine may possibly be a dialkylamidophenylquinoline, and that the second benzene nucleus is present in a partially hydrogenated form.

W. P. W.

Strychninesulphonic Acids. By C. STOEHR (*Ber.*, 20, 2733—2734).—A note calling attention to the fact that the results obtained by Guareschi (Abstr., 1887, 853) are essentially the same as those previously arrived at by the author (Abstr., 1886, 269).

W. P. W.

Peculiar Modification of Urobilin. By E. SALKOWSKY (*Chem. Centr.*, 18, 1089).—On examination of a sample of urine peculiarly rich in urobilin, it was observed that on keeping this colouring matter disappeared without any marked change of the colour of the urine. This conversion of the urobilin seems not to be conditioned by the ammoniacal fermentation of the urine or by the presence of micro-organisms. Urobilin is a substance readily decomposed, and passes into a modification which, although still coloured, shows no absorption-bands, nor fluorescence with zinc chloride in ammoniacal solution, and is not taken up by chloroform. It is probable that in most normal urines, urobilin, as well as its decomposition-products, is present.

V. H. V.

Chemical Formation of Albumin. By C. F. W. KRUKENBERG (*Chem. Centr.*, 1887, 1085).—When keratin, previously purified by the action of pepsin and trypsin, is heated with water in a sealed tube, it dissolves to form an alkaline liquid, possessing a strong odour of hydrogen sulphide. This liquid contains a non-dialysable substance, keratinose, precipitated by ammonium sulphate, which agrees with hemialbumose as regards these reactions, although it does not give the hydrochloric acid test. Keratinose is converted by pepsin and hydrochloric acid at a blood-heat into keratinpeptone, which is not precipitated by ammonium sulphate. Under the same conditions spongin yields *spongionose*, a soluble, indiffusible substance; this is also converted into spongiopeptone. By the decomposition of spongin, carbamide seems to be formed. The author considers that the albuminoids and skeletins are related to albumin as methyl to methyl ether.

V. H. V.

Coagulation of Albumin. By V. MICHAÏLOFF (*Chem. Centr.*, 1887, 1088).—According to the author the coagulation of albumin is due to one of two phenomena, namely, the true coagulation induced by the action of ferments or heat, a process analogous to etherification or the formation of polyhydro-silicates or glycols, and a pseudo-coagulation caused by a loss of "gelatinose-water," which corresponds with the loss of water of crystallisation of salts. The coagulating power of salts on solutions of albumin is dependent on the nature of the acid and base therein contained; the maximum effect is produced by ammonium, the mean by sodium, and the minimum by potassium salts. Again, in the case of ammonium salts, the sulphate is more

efficient than the nitrate, and of potassium salts the sulphate than the chloride.

V. H. V.

Egg Albumin and Albumoses. By R. H. CHITTENDEN and P. R. BOLTON (*Studies from Lab. Physiol. Chem., Yale Univ.*, **2**, 126—155).—These experiments were designed to contrast the products of digestion of egg albumin with those obtained by Kühne and Chittenden from fibrin. Four samples of albumin were prepared; in some cases it was separated from globulin by saturation with magnesium sulphate, in others by dilution and the subsequent addition of acetic acid. An elementary analysis of these four samples gave the following average percentages:—C, 52·18; H, 6·93; N, 15·81; S, 1·87; O, 23·21. Further, coagulated products did not differ in composition from non-coagulated albumin. These results do not agree with any of the formulæ ascribed to albumin by previous observers.

Peptic digestion of the albumin resulted in the formation of albumoses of which the percentage composition and reactions were determined. In composition they were found to differ from each other somewhat more than the albumoses from fibrin; collectively, however, there is less difference in composition between the albumoses and the egg albumin from which they were formed than in the case of the albumoses from fibrin. The following table gives the final results:—

	Fibrin products.			Egg albumin products.		
	Proto-albumose.	Deutero-albumose.	Fibrin.	Proto-albumose.	Deutero-albumose.	Egg albumin.
C	50·77	50·65	52·68	51·07	51·62	52·33
H	6·78	6·83	6·83	6·98	6·97	6·98
N	17·14	17·17	16·91	16·00	15·82	15·85
S	1·08	0·97	1·10	1·95	1·96	1·82
O	24·23	24·38	22·48	24·00	23·63	23·02

In their reactions the different albumoses (proto-, deutero-, hetero-, and dys-albumose) obtained from egg albumin do not differ essentially from those obtained from fibrin.

W. D. H.

Metallic Compounds of Albumin and Myosin. By R. H. CHITTENDEN and H. H. WHITEHOUSE (*Studies from Lab. Physiol. Chem., Yale Univ.*, 95—125).—Many researches on the subject of the metallic compounds of albumin have been carried out since Lieberkühn attempted to establish the molecular weight of albumin by the analysis of copper albuminate. The more recent work of Harnack (*Abstr.*, 1882, 747) showed that two compounds of albumin (from white of egg) with copper occur, one containing 1·35 per cent., and the other 2·64 per cent. of copper. In the present research, albumin was freed from globulin by the use of dilute acetic acid, and both the

acetate and sulphate of copper were used in the preparation of the albuminate. The precipitate was well washed with water, powdered, and dried. The percentage of copper was first determined as cupric oxide by ignition and weighing: the oxide was then dissolved in dilute nitric acid, treated with hydrogen sulphide, and the amount of cuprous sulphide obtained weighed. By the former method, in 15 preparations the average result was 1.17 per cent. of copper; and by the latter method 0.94 per cent.; the preparations, therefore, contain 0.23 per cent. of ash. In order to obtain less ash, Harnack dissolved the albuminate in sodium carbonate and reprecipitated it by the careful addition of acid; this process was repeated several times. This treatment certainly increases the percentage of copper, but is a source of error, as the sodium carbonate withdraws a portion of the albumin. Long-continued washing with water also causes partial dissociation of the compound. The results obtained correspond with the formula $(C_{72}H_{112}N_{18}SO_{22})_4 + Cu - H_2$.

A normal lead salt causes a small precipitate when added to albumin, whilst with basic lead acetate the albumin is completely precipitated. This confirms the previous statement of Berzelius (*Lehrbuch der Chemie*, 9, 29). The preparations were well washed from both lead and albumin, dried, and the lead was determined, first by simple ignition, and then obtained as sulphate, which was ignited. The results indicate that more than one compound of lead is formed, that made by the addition of a large excess of the basic acetate, containing about five times as much lead as the ordinary basic lead compounds. An iron compound which was found to be more stable than the copper albuminate, and corresponded fairly well with the formula $(C_{72}H_{112}N_{18}SO_{22})_4 + Fe - H_3$, and a zinc compound, $(C_{72}H_{112}N_{18}SO_{22})_4 + Zn - H_2$; acid compounds with uranium, $(C_{72}H_{112}N_{18}SO_{22})_3 + U - H_2$; with mercury, $(C_{72}H_{112}N_{18}SO_{22})_4 + Hg - H_2$; and with silver, $(C_{72}H_{112}N_{18}SO_{22})_3 + Ag_2 - H_2$, were also prepared and analysed. Much stress is not laid on such formulæ; as it seems possible to form a large variety of compounds by simply modifying the conditions of precipitations. This, with the undoubted tendency of the compounds to dissociation, may account for the lack of agreement in the results of different workers. Similar compounds prepared from myosin obtained by extracting ox flesh with 15 per cent. ammonium chloride were prepared, and the percentage results show that these two forms of proteid matter do not form corresponding compounds with the metallic salts used. This is illustrated by the following table:—

	Egg albumin.	Myosin.
Copper compound	0·94 per cent. Cu	1·17 per cent. Cu
Iron „	0·95 „ Fe	2·29 „ Fe
Zinc „	0·91 „ Zn	0·72 „ Zn
Uranyl „	4·60 „ U	7·49 „ U
Mercury „	2·89 „ Hg	2·43 „ Hg
Lead „	2·56 „ Pb	—
Silver „	4·09 „ Ag	—
Nickel „	—	4·70 „ Ni
Cobalt „	—	6·03 „ Co

W. D. H.

Casein and Caseoses. By R. H. CHITTENDEN and H. M. PAINTER (*Studies from Lab. Physiol. Chem., Yale Univ.*, **2**, 156—199).—Danilewsky (*Zeit. physiol. Chem.*, **7**, 433) has asserted that casein is a mixture of two proteids, caseoprotalbin, partially soluble, and caseoalbumin, insoluble in hot 50 per cent. alcohol. Hammarsten (*ibid.*, **7**, 227) has shown that the peculiar behaviour of Danilewsky's casein is due to its containing calcium phosphate, the presence of which impurity depends on the use of hydrochloric acid in the precipitation of the casein, as this acid does not favour the removal of the salt as well as acetic acid. He also considers that casein is a single proteid. In the present research, seven distinct preparations of casein were made. Elementary analyses show a close agreement throughout, and the results moreover accord closely with those of Hammarsten.

In the digestion of casein with hydrochloric acid, peptones are ultimately formed, and the name caseose is given to the intermediate products. These were separated by the methods of Kühne and Chittenden into proto-, hetero-, and deuterocaseose, which correspond with the albumoses with similar names. The quantity of heterocaseose obtained was usually very small. The reactions characteristic of albumoses apply generally to the caseoses. Unlike proto-albumose however, *protocaseose* is precipitated from aqueous solutions by acetic acid. The average of the analyses of 10 preparations of *protocaseose* gives the following percentage results:—

	C.	H.	N.	S.	O.
Protocaseose	52·89	7·10	15·94	0·95	23·12
Casein	53·30	7·07	15·91	0·82	22·03

Deuterocaseose contains a smaller percentage of carbon than *protocaseose*, and *heterocaseose* contains fully as much carbon as casein itself.

An insoluble, semi-gelatinous substance which separates in the first stage digestion has not yet been investigated. Weyl's commercial "casein-peptone" contains large quantities of caseoses.

W. D. H.

Animal Tannin. By M. VILLON (*Chem. News*, **56**, 175).—Corn weevils (*Calandra granaria*) were killed, ground in a mortar, and digested for one hour in boiling 90 per cent. alcohol. The residue from the evaporation of the extract is taken up with ethyl acetate at 50°, and precipitated by means of ammoniacal zinc acetate. The precipitate is decomposed with oxalic acid, and the solution evaporated in a vacuum. In this way 3 per cent. of a substance having all the general properties of tannin is obtained from the weevils. This animal tannin, *fracticornitannin*, forms small reddish-yellow scales.

D. A. L.

Physiological Chemistry.

Influence of some Organic and Inorganic Substances on Gas Metabolism. By R. H. CHITTENDEN and G. W. CUMMINS (*Studies from Lab. Physiol. Chem., Yale Univ.*, **2**, 200—236).—The question investigated was the consumption of oxygen and the elimination of carbonic anhydride. The animal, a rabbit, was confined in a large bell-jar, through which air was drawn by means of three aspirators, which were arranged to work evenly, and emptied themselves in half an hour. Two-fifths of the mixed air was drawn successively through three absorption-tubes, each of which contained 100 c.c. of standard baryta. The carbonic anhydride was estimated by titration with standard oxalic acid. The results obtained are not absolute, but express quite well the comparative action of the various substances experimented with. It was found necessary to have the animal in a state of hunger during an experiment. Accordingly it was deprived of food for three days previous to the experiment, as well as during the three days for which the experiment lasted. During the last two of the three days, the substance experimented with was given in small and oft-repeated doses. Every day numerous determinations of carbonic anhydride were made, and comparison could then be made between the normal excretion of that substance and that during the administration of the drug. Observations were also made on the body temperature. The following are briefly the results obtained with the following substances:—Uranyl nitrate acts slowly, but when taken in sufficient quantity tends to raise materially the body temperature, and increase very noticeably the excretion of carbonic anhydride. Copper sulphate shows a marked influence in depressing body temperature, and a still greater influence in diminishing the production of carbonic anhydride. Arsenious oxide given in non-toxic doses also diminishes the excretion of carbonic anhydride, presumably through its action on the metabolic activity of the tissue cells. Tartar emetic acts similarly. Morphine sulphate has but little action; a slight fall in the excretion of carbonic anhydride immediately after a dose must be attributed to the semi-somnolent condition of the animal. Quinine sulphate, which is so important as an antipyretic, is found in a healthy hungry rabbit

to have only a very slight depressing influence on body temperature, and a minimum effect on the production of carbonic anhydride. Cinchonidine sulphate produced a slight rise of temperature and a gradual diminution in the amount of carbonic anhydride excreted; it also caused tetanic convulsions and finally death. Antipyrine had little effect, the only change being a fall in temperature just before death.

W. D. H.

Action of Uranium Salts on Digestive Ferments. By R. H. CHITTENDEN and M. T. HUTCHINSON (*Studies from Lab. Physiol. Chem., Yale Univ.*, 2, 55—67).—Very small quantities of uranium salts promote the activity of saliva; larger amounts hinder and finally stop its amylolytic action. 100 c.c. of digestive mixture contained 2 c.c. of neutralised saliva, and 1 gram of pure potato-starch. The mixture was warmed at 40° for 30 minutes and then boiled to prevent further action; the amount of sugar present was estimated as dextrose by Fehling's solution. This was compared with other digestive mixtures to which a certain percentage of a uranium salt was added. The following table illustrates the results obtained with uranyl nitrate:—

Amount of salt added.	Total amount of reducing substances.	Starch converted.	Relative amylolytic action.
0·000 per cent.	0·4135 gram.	37·21 per cent.	100·0
0·001 "	0·4083 "	36·74 "	98·7
0·003 "	0·3873 "	34·85 "	93·6
0·005 "	0·3698 "	33·28 "	89·4
0·001 "	0·3612 "	32·50 "	87·3
0·003 "	0·3131 "	28·17 "	75·5
0·008 "	trace	—	—

Uranyl acetate was more inhibitory in its action, due possibly to its greater acidity; 0·0003 per cent. increases, 0·003 per cent. stops amylolytic action. Experiments with similar results were obtained with ammonio-uranous sulphate, sodio-uranic sulphate, potassio-uranic oxychloride, and ammonio-uranic citrate. The action of the salts varies with different specimens of saliva, according to the amount of proteid present which is precipitated by them. Loss of amylolytic power is due in part to partial direct destruction of the ferment as well as to change in reaction of the fluid. There must, however, be something in addition to the mere presence of these salts dependent on chemical constitution that controls the action of the ferment.

The same salts were also investigated in regard to their action on the proteolytic action of pepsin-hydrochloric acid. Similar series of experiments were made, and the results compared by estimating the amount of fibrin left undigested after an hour's action. The potassium uranic oxychloride was the only salt that produced initial stimulating action on the ferment; the others all retarded its activity. The difference in action of the various salts seems to depend on the

acid liberated from them; the acids which are not capable of working with pepsin will most readily retard gastric digestion; thus the acetate retards digestion more than the nitrate; acetic acid mixed with pepsin is practically inactive, whilst nitric acid is about four-fifths as active as hydrochloric acid.

A similar series of experiments showed that uranium salts also retarded the action of the pancreatic ferment. W. D. H.

Digestion in Rhizopods. By M. GREENWOOD (*Journ. of Physiol.*, **8**, 263—287).—The authoress has continued her observations on the digestive processes in *Amœba* and *Actinosphærium* (Abstr., 1886, 1053) with the following results: (1.) The ingestion of solid matter is promiscuous in amœba, that is nutritious and innutritious matters are taken in with equal readiness. Actinosphærium, on the other hand, rarely ingests innutritious particles. (2.) The act of ingestion in amœba is accompanied by the emission of pseudopodia; in actinosphærium these may or may not be thrown out. (3.) The nutritious matter taken in by amœba is not surrounded by fluid when it lies in the endosac. (4.) Nutritious particles are in both animals digested by fluid poured out around them. This fluid has no action on the cuticle of organisms, or on cellulose or siliceous cell-walls. Fat and starch are apparently not digested by it. It is a colourless fluid, which acts on coagulated, and still more so on non-coagulated proteid matter. It has no action on litmus or carmine particles, accidentally enclosed with nutritious particles, and is therefore neutral in reaction. (5.) The secretion is more active in actinosphærium than in amœba. (6.) Chlorophyll is changed to a dark-brown colour by amœba; this is not so marked in actinosphærium. (7.) Ejection is performed at the hind end of amœba, either by means of a vacuole, or often in the case of algæ without one. An excretory vacuole is always present in actinosphærium. (8.) The time between ingestion and ejection is difficult to determine, and varies with the size and digestibility of the ingesta; it averages 3 to 4 days in amœba. In actinosphærium the digestive act is shorter and occupies from 1½ to 8 hours. W. D. H.

Dehydration of Glucose in the Stomach and Intestines. By R. H. CHITTENDEN (*Studies from Lab. Physiol. Chem., Yale Univ.*, **2**, 46—53).—Pavy (*Chem. News*, **49**, 128, 140, 155, 162, 172, 183) brought forward evidence to show that there exists, particularly in the stomach and intestines of rabbits, a ferment which has a dehydrating action on glucose, transforming it into a substance with less cupric oxide reducing power, akin to maltose. This substance is formed at a temperature of 48° by bringing a solution of glucose into contact with the stomach and intestines of a rabbit; by boiling it with dilute sulphuric acid, it is again converted into glucose. In the present research these experiments were repeated, but gave an entirely negative result, rabbits and cats being the animals used, in different stages of digestion. Ogata (*Jahrsber. für Thierchem.*, **15**, 275) has also been unable to confirm Pavy's results. W. D. H.

Influence of Antimonious Oxide on Metabolism. By R. H. CHITTENDEN and J. A. BLAKE (*Studies from Lab. Physiol. Chem., Yale Univ.*, **2**, 87—94).—Antimonious oxide was used instead of tartar emetic, because of its probable slower toxic action, and also because it has been so extensively used as a means to induce or to aid in the production of fatty degeneration, for instance, in the production of fatty livers in geese (H. C. Wood, *Therapeutics*, 161).

The nitrogen, phosphorus, sulphur, and chlorine were estimated daily in the urine of a dog, to whom a fixed diet was administered, first for a period without and afterwards for a period with the addition of small quantities of antimonious oxide. The results of the two series may be stated as follows:—

Daily Average of Constituents of Urine in grams.

	Nitrogen.	Phosphorus.	Sulphur.	Chlorine.
1. Without antimony	11·743	0·7251	0·6708	0·5592
2. With antimony	12·028	0·7292	0·6534	0·5070

The conclusion is drawn that small repeated doses of antimonious oxide are without influence on the excretion of nitrogen, sulphur, and phosphorus, and that consequently this compound, at least when taken in non-toxic doses, has no action on proteid metabolism.

W. D. H.

Asparagine as a Nourishing Constituent of Food. By H. WEISKE (*Landw. Versuchs-Stat.*, **34**, 303—310).—A review of the work done by various chemists. It is shown that the mass of evidence produced is in favour of asparagine being a nutrient for herbivora, and that under appropriate conditions it prevents waste, and causes the formation of albumin. As to its influence on omnivora and carnivora, this does appear to be the case, but on the contrary it produces strong diuretic action, and destruction of albumin; however, more experiments are necessary for the complete elucidation of the problem.

E. W. P.

Ash in Bones of Different Ages. By W. P. MASON (*Chem. News*, **56**, 157—159).—The author has examined for ash and as to brittleness several samples of bones, both from males and females, from bodies recently dead and from living people (amputations). In all cases the history of the bone was known, and the ash determined in portions selected from the dense portion of the middle of the shaft of the femur. All diseased bones, or bones from persons suffering from ailments affecting the bones, were excluded. His results show that from manhood to old age, there is no variation in the amount of ash in bones. That the brittleness of old bones is due to the material rather than the structure; that it is not therefore due to the increase of spongy tissue and diminution of the denser portions of the bone as age advances (Frémy's supposition); nor does it arise from the increase in the percentage of inorganic salts.

D. A. L.

Distribution of Antimony in the Organs and Tissues. By R. H. CHITTENDEN and J. A. BLAKE (*Studies from Lab. Physiol. Chem., Yale Univ.*, 2, 68—86).—These experiments were undertaken in order that data of medico-legal importance might be obtained; the relative distribution of the poison in the tissues giving indications of the length of time that intervenes between the administration of the poison and death. The only trustworthy method of estimating small quantities of antimony was found to be the electrolytic method (Classen, *Abstr.* 1885, 191, 932); preliminary experiments were performed which showed that this method acts well when antimony is mixed with organic matter, and also in urine. A feeble current was used and allowed to act for many hours; the antimony was collected at the negative pole which was a platinum capsule. When the separation of the metal was complete, it was found necessary to remove all organic matter by washing with water before breaking the current, otherwise the antimony quickly redissolved.

Tables are given of the results in which various compounds of antimony were given by hypodermic injection, by the mouth, and by the rectum in dogs and rabbits. The brain and liver were the organs in which the metal tends most to accumulate, although if sufficient time elapses between the giving of the poison and death, it tends to spread more uniformly through the body; the more soluble compounds of antimony like tartar emetic produce their effects more rapidly than the insoluble forms like antimonious oxide.

W. D. H.

Formation and Elimination of a Ferruginous Pigment in Poisoning with Toluylenediamine. By ENGEL and KIENER (*Compt. rend.*, 105, 465—467).—In acute cases which end in death in a few hours, there is no ictericia and no hæmoglobinuria, but the victim falls into a state of coma and dies. There is intense congestion of all the organs and especially of the lungs, but the spleen and marrow contain no excess of pigment.

When death ensues after a few days, there is always ictericia and often hæmoglobinuria, and the urine is loaded with fat and yellow and brown pigment granules which are variable in composition but sometimes contain iron. The ferruginous pigment formed by the destruction of the hæmoglobin accumulates in the spleen and marrow. It seems to be formed from the hæmoglobin in the protoplasm from the cellules and not from the red corpuscles. The deposits in the liver are less constant and more local.

In chronic cases ending in death after several weeks, the ictericia is moderated and is often retarded for a long time. There is no hæmoglobinuria and no granular pigment in the urine. The animal eventually succumbs to anæmia, which is followed by coma, and after death the spleen, marrow, and liver contain a greater quantity of the ferruginous pigment than in acute cases, and there is a notable quantity in the kidneys and in the lymphatic ganglions of the abdomen.

C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Formation of Nitrites during Nitrification of Ammoniacal Solutions. By J. M. H. MUNRO (*Chem. News*, 56, 62—64).—Gayon and Dupetit have suggested that the nitrite formed during nitrification is produced by reduction of previously formed nitrate; they suppose the nitrifying organism either to acquire reducing powers by living at the bottom of a solution, or else that it is not pure but mixed with denitrifying bacteria, and that the nitrate reduced by one or other of these, supplies oxygen for the oxidation of organic matter present in the solution. The present experiments disprove this and show (1) that a solution of potassium nitrate, seeded with soil from a recently nitrified solution, develops no nitrite even though kept for a year in a stoppered bottle; (2) that a solution of ammonium chloride, seeded with the same soil, and with no other added organic matter, formed nitrite in increasing quantities from the third day to the 139th, when almost all the ammoniacal nitrogen was present in that form, afterwards passing into nitrate; (3) that a solution containing both potassium nitrate and ammonium chloride ($3\text{KNO}_3 + \text{NH}_4\text{Cl}$) seeded with the same soil, ran through exactly the same course as the preceding. If an organism were present capable of reducing nitrate to nitrite with simultaneous oxidation of ammonia to nitrite, four times the quantity of nitrite produced in the preceding case could theoretically be formed: instead of this, the amounts were almost exactly equal, and both a little under that corresponding to the whole of the ammoniacal nitrogen. The author concludes that the nitrite is formed by oxidation of the ammonia.

J. M. H. M.

Chemical Nature of Aristolochia Serpentaria. By M. SPICA (*Gazzetta*, 17, 313—316).—The *Aristolochia serpentaria* (Virginia snake-root) grows in the southern part of North America, especially in the mountainous districts of Carolina and Virginia; various preparations of its roots are used medicinally as febrifuges. Its chemical nature has previously been examined by Buchholz, Chevallier, and others, who have obtained besides other products a volatile oil. On distilling the ethereal extract of the root in a current of steam, a yellowish-green oil is obtained, heavier than water, and having an odour resembling that of camphor and valerian. This oil, after treatment with potash, is cooled by a freezing mixture, which causes the separation of a crystalline stearoptene; this melts at 198° , boils at 212° , and is shown by chemical analysis and its physical properties to be borneol. No very definite product could be obtained from the oil from which the borneol had thus been separated.

V. H. V.

Constituents of Scopolia Root. By H. HENSCHKE (*Chem. Centr.*, 1887, 1087—1088).—*Scopolia japonica*, or Japanese belladonna,

is a species of Solanaceæ indigenous to Japan and China. Two alkaloids are manufactured commercially from its roots, namely, scopoleïne and rotoïne, and Eijkman has obtained two substances, a glucoside, scopolin, and scopoletin, its decomposition product. It is here shown that the root of the plant contains no peculiar alkaloid, but the three mydriatic alkaloids, atropine, hyoscyamine, and hyoscyne in variable proportions.

Commercial rotoïne is not a distinct base, but a mixture of the sodium salts of fatty acids of high molecular weight. The fluorescent substance, scopoletin, obtained by Eijkmann, is identical with the so-called chrysotropic acid of Kunz, whilst it is further probable that it is identical with methylæsculetin. V. H. V.

Oil of Lallemantia Iberica. By L. RICHTER (*Landw. Versuchs-Stat.*, 34, 383—390).—The oil expressed from the seeds of *Lallemantia iberica* (Fisch et May) has the property of being the most rapidly “drying” of all known oils. The ethereal extract of the seeds may be completely decolorised by animal charcoal, and on evaporation of the ether, a pale-yellow oil is obtainable which after some time becomes slightly opaque; the opacity may be removed by filtration, when a clear fat of faint but acrid odour, whose taste resembles that of linseed oil, is left on the filter. The oil is insoluble in cold, but readily soluble in hot alcohol, insoluble in cold acetic acid (1·0643). The sp. gr. of the oil is 0·9336 at 20°, and its solidifying point —35°; the free fatty acids melt at 22·2°, and resolidify at 11·0°. When exposed to the air for five days, a crust is formed at the edge of the liquid, but complete resinification, or “drying,” occurs in 24 hours, after it has been heated at 150° for three hours. Casselman states that complete drying of linseed oil only occurs after 36 to 48 hours’ heating at 150°; poppy oil requires four to five days, and hemp oil still longer.

It behaves towards nascent nitrous acid in the same manner as linseed oil, a dark-red doughy mass being produced. Mixed with concentrated sulphuric acid, the temperature rises to 102° and even to 120°.

According to v. Hübl’s method, the oil purified from fat, unites with 162·1 grams of iodine per 100 grams oil, whilst the fat combines with 166·7 grams of iodine. No other oil approaches closely to this figure except linseed. As the absorption of iodine by the oil corresponds with its facility for drying, it was necessary to estimate the amount of oxygen absorbable; this was done by Livache’s process, when it was found that the oil absorbed 15·81 per cent. of oxygen in one day, whilst the fatty acid absorbed 16·58 per cent. in 28 days; linseed absorbs 14·3 per cent. in two days, and its fatty acid 11 per cent. in eight days. Hehner’s and West-Knight’s methods for determining the percentage of insoluble fatty acids in the oil were both used, the former method showed the presence of 93·3 per cent., and the latter 94 per cent., and the volatile oil (Reichert’s method) amounted to 1·55. The figures representing saponifiability (Köttstorfer) were 184·9 (milligrams KHO), and 9·75 per cent. of glycerol was found, corresponding with

99.74 per cent. of glycerides. The lead salt was used to cause separation of the liquid and solid fatty acids, when it was found that of the latter there was 6.55 per cent. and of the former 93.45 per cent. present.

The quantitative reactions are given in the original.

When grown as a field crop, *Lallemantia* yielded 2031 kilos. seed and 6314 kilos. straw per hectare.

E. W. P.

Are Nitrates indispensable for the Growth of Field Crops ?

By O. PITSCH (*Landw. Versuchs-Stat.*, **34**, 217—258).—The carefully conducted experiments for the elucidation of the above question appear to be most satisfactory, and the decision arrived at is that at any rate barley, oats, beans, and wheat can and do grow in a soil absolutely destitute of nitrates, free from all nitrifying bacteria, but in which nitrogenous manures are present as ammonium sulphate. The experiments were made during two seasons, and all the precautions taken, the progress of the various plants grown, and the apparatus employed are fully detailed. In outline, a rich soil was first heated in an oil-bath to destroy all bacteria, then thoroughly washed by upward displacement, to free it from all nitrates, again heated and then placed, the first year, in large beaker glasses, and in the second season in iron vessels 62 cm. \times 25 cm.; the seeds were sown, and a thick covering of cotton wool placed on the surface of the soil in a suitable holder of wire net, so as to prevent access of all aerial spores; distilled water was used for watering by a special method described in full, whereby the water was admitted from below. Two sets of such vessels and seeds were employed. To the soils used in the first year, bicalcium potassium phosphates and ammonium sulphate were added, both to the original and to the parallel sets, the difference between the two being that the soil of the parallel sets was neither heated nor covered over with cotton wool. In the second year, however, the soil underwent the same process in both sets, but in place of ammonium sulphate being added to the controlling sets, sodium nitrate was added, and no cotton wool used. The results in both years were, however, similar, namely, that the growth of the plants under such peculiar conditions as total absence of nitrates was not largely affected—certainly there was a difference, but not at all remarkable; the plants were able to grow healthily, but perhaps not robustly without any nitrates. It was noticed that those plants which could obtain no nitrates, but had to be content with nitrogen in other forms, came to a standstill for a short time early in their growth, and after a short period of rest, again grew normally. The author tried to account for this in the first year, by the fact that as the manure had not been mixed thoroughly with the soil throughout its whole depth, the lower roots were unable to obtain nitrogen, consequently no growth was made until new roots were formed higher up, but after the experiments of the second season had been made, he was obliged to abandon this theory, for although he had mixed the manure thoroughly with the soil, yet this arrest of growth again occurred, whilst no such effect was produced in the soil containing nitrates.

E. W. P.

Agricultural Experiments. By J. RAULIN (*Compt. rend.*, 105, 411—414).—In order to avoid, in agricultural experiments, errors due to differences between the natural fertility of contiguous patches of soil, the experimental plot should be divided into three rectangular sections, A, B, and C, which are treated separately. As a rule, the results with A and C differ, and in a few cases the differences are quite irregular. Usually, however, the fertility of the plot varies gradually, so that the mean of A and C is practically identical with B.

Experiments made in this way show that superphosphates and precipitated calcium phosphate produce a distinct increase in the wheat crop, whilst with fossil phosphates and with slags the results are doubtful, the apparent increase not being greater than the variations between the three sections of the plot. C. H. B.

Analytical Chemistry.

Grinding Mill for Minerals. By K. ZULKOWSKY (*Ber.*, 20, 2664—2669).—A description of a mill in which minerals may be readily reduced to fine powder. The grinding surfaces are of agate, and the pestle is so arranged that it can be rotated by a water-motor against the lower surface with a pressure capable of being varied at will. The material, already reduced to the coarseness of sand, is introduced into the mill through a sector cut in the pestle.

W. P. W.

Determination of Sulphur in Pyrites. By J. W. WESTMORELAND (*J. Soc. Chem. Ind.*, 6, 84—87).—It is shown that the results obtained by Lunge's "old process" (precipitation of the sulphur from ferric solutions), agree closely with those given by the new process (precipitation after separation of the ferric oxide by ammonia), which is therefore a needless elaboration. The new method is also liable to losses caused by an extra filtration and washing, and by sulphur retained in the ferric oxide, whilst sulphur is liable to be introduced by the ammonia and hydrochloric acid employed. The results obtained by Lunge's processes express the total percentage of sulphur in Spanish pyrites; it is, however, necessary to use only a moderate excess of barium chloride for precipitation, great care being taken in the use of hydrochloric acid when washing this precipitate.

D. B.

Estimation of Sulphur in Pyrites. By G. LUNGE (*J. Soc. Chem. Ind.*, 6, 96).—The author criticises Welch's process (*Abstr.*, 1887, 180) for assaying iron pyrites for sulphur available for sulphuric acid manufacture, and shows that the experiments having been made with impure lead sulphide are not conclusive.

D. B.

Kjeldahl's Method of Estimating Nitrogen. By F. W. DAFERT (*Landw. Versuchs. Stat.*, 34, 311—353).—In this article, are detailed

in full the results of experiments made for the purpose of testing the value of Kjeldahl's process for estimating organic nitrogen, and of an examination of the various modifications of this process, as recommended by Kreusler and others.

Estimation by the Original Process.—Certain nitrogenous compounds only seem to yield their nitrogen in the ammoniacal forms, the result being that the process is inaccurate with regard to others; of the latter class, anilines and hydrazines are special examples, but some compounds, contrary to expectation, yield their nitrogen as ammonia more readily than others; as for instance, it was expected that hydrazines would yield ammonia more completely and quickly than nitro-compounds, but the contrary is the case.

The Action of the Sulphuric Acid.—To aid the solution of this question, Kreusler's modification, where phosphoric anhydride is added to the sulphuric acid, was employed; sugar was also added. The explanation which is given is, that the sulphuric acid removes from the substance the elements of water and of ammonia, and the sulphurous anhydride formed in the reaction reduces the nitrogenous compound; the addition of organic matter (sugar) to the nitrogenous compound slackens the formation of ammonia when the compound is not volatilised by the acid; consequently to obtain quantitative results, the sulphuric acid must not volatilise the compound, nor completely decompose it, for the analysis of some substances by this method free nitrogen accompanies the ammonia.

The Action of Permanganate.—The presence of the permanganate when used in company with the mixture of acids, causes a destruction of the organic matter present, the nitrogen being so separated that nearly the whole of it is transformed into ammonia; as a rule this modification of Kjeldahl's process may be employed for all quantitative analyses, but it is necessary that the mixture shall be thoroughly and sufficiently heated.

The Addition of Metallic Salts.—This modification of Wilfarth's renders the original process more rapid, although the time required for the analysis is shortened very considerably by the addition of mercury, it is at the cost of accuracy; it should only be introduced in those cases where very stable compounds are under examination, or also when the compounds readily give up their nitrogen as ammonia. From careful examination, it appears that the discrepancies which exist between the results obtained by Kjeldahl's original method, Wilfarth's and Ulsch's (addition of platinum chloride), are due to loss of nitrogen as nitrogen, and not to an insufficiency of heating, when the compound is only slightly stable. The author considers that Wilfarth's explanation of the reaction which occurs when metallic salts are present, is satisfactory, but he also adds that when those compounds which do not resist the action of sulphuric acid well, or which are readily oxidised, are dealt with, the addition of the metallic salt causing violent oxidation, ammonia may be in part replaced by nitrogen; increasing the quantity of platinum, addition of oxygen and mixing with organic substances may also result in loss, even when the compound is not easily decomposed. Mercury should be always employed when very stable compounds are to be analysed; amines

and alkaloïds resist oxidation, but Ulsch's process must not be used because of its uncertainty, except in special cases, for example, with potassium nitrate.

General Application.—Nitrogenous compounds may be divided into two classes as regards the applicability to them of Kjeldahl's process of analysis. In the first are placed those which can be analysed without any previous treatment, for example, all amides and ammonium bases, pyrroline and quinoline compounds, alkaloïds, bitter substances, albuminoids and their allies, and perhaps the indole group; whilst to the second class belong all nitro-, nitroso-, azo-, diazo-, hydrazo-, and azoamido-compounds, nitrates and nitrites, the hydrazines, and possibly the cyano-compounds. Two methods may be employed for the previous treatment of this second class: addition of an organic substance, or reduction with zinc-dust, and even the two combined, but the choice of which is to be used must rest with the analyst. This uncertainty will for the present preclude Kjeldahl's process, or its improvements, from supplanting Dumas's older and exact method. For the estimation of nitro-compounds, it is recommended to dissolve the substance in 10 c.c. of alcohol (or if it is very stable, directly in sulphuric acid) decompose by zinc-dust, add 10 c.c. of acid, and warm until all alcohol is got rid of; when this is accomplished, add 10 c.c. of the acid mixture together with mercury, and then proceed as with an ordinary compound. When distilling with sodium hydroxide, special care must be taken to avoid shaking the flask; it is therefore advisable to apply heat by means of a sand-bath; in the same manner nitroso- and azo-compounds may be readily analysed. Hydrazo-compounds must first be converted into azo-compounds, before exposing them to the action of the sulphuric acid. The author, for example, heats the sulphate of phenylhydrazine first with excess of cane-sugar in presence of sodium acetate for some hours on a water-bath; after drying the resulting mass, the acid may be added. Most cyano-compounds, as far as the author is aware, can be analysed by this process, but some may exist which will not bear the method.

E. W. P.

Notes on Nesslerising. By J. M. MILNE (*J. Soc. Chem. Ind.*, **6**, 33).—The author recommends Hehner's method in which the nesslerising is conducted in graduated cylinders having a somewhat broad foot, a glass tap being fused into their sides near the bottom, so that the solution, either standard or water distillate, may be run out until the two tints correspond. This method, a description of which was given in *Chem. News*, **33**, 185, is very simple and readily carried out. As nesslerising cannot be done in gaslight, the author proposes to imitate the process with two shades of indigo solution. D. B.

Estimation of Ammonia in Soils by the Knop-Wolf Method. By A. BAUMANN (*Landw. Versuchs-Stat.*, **34**, 259—276).—A reply to Knop (*ibid.*, **33**, 438).

Moisture and Free Acid in Superphosphates and similar Fertilisers. By J. RUFFLE (*J. Soc. Chem. Ind.*, **6**, 327—333).—It is

shown that the soluble phosphoric acid existing in superphosphates is not entirely present as monocalcium phosphate, and that exposure to 100° drives off more than the true moisture, that is, the adhering uncombined water. It is recommended to determine the moisture in the following manner:—Weigh out 2 to 5 grams of the superphosphate in its natural state on a double watch-glass, place under an air-pump over dry calcium chloride, exhaust, then leave for 18 to 24 hours and weigh. The author shows that the acidity of ordinary superphosphates and ammoniated superphosphates is due to phosphoric acid, and not to sulphuric acid. In ammoniated superphosphates, monocalcium phosphate is substantially absent, the free acid being phosphoric acid.

D. B.

Detection of Small Amounts of Carbonic Anhydride and other Gases. By O. RÖSSLER (*Ber.*, 20, 2629—2631).—A small test-tube is drawn out at the lower end to a capillary; this is bent upwards, and cut off at a distance of 1 cm. from the bend. A capillary funnel is then made of such a size that the upper end fits the test-tube, the lower end being at a distance of 1·5 to 2 cm. from the bottom. The substance to be tested for carbonic anhydride is put into the outer tube, the capillary funnel containing baryta-water fitted, and the lower end of the apparatus then dipped into hydrochloric acid. With 0·0005 gram of sodium carbonate a very distinct turbidity, with 0·00005 gram a distinct turbidity is produced in the drop of baryta-water at the end of the capillary. It is possible to detect 0·02 milligram of carbonic anhydride. Sulphuric and nitric acids, hydrogen sulphide, ammonia, &c., can also be detected by means of the apparatus, using iodide of starch, ferrous chloride, lead acetate, and copper sulphate respectively. A sketch of the apparatus is given.

N. H. M.

Absorption of Carbonic Oxide by Cuprous Chloride. By H. DREHSCHMIDT (*Ber.*, 20, 2752—2755).—Hempel has recently shown that in certain cases when cuprous chloride is used as an absorbent of carbonic oxide in gas analysis, there is an increase instead of a decrease of volume. This result is explained on the supposition that the ethylene contained in the absorption-liquid is driven out by the absorbed carbonic oxide. It is here shown that this explanation is not sufficiently valid, as similar results were obtained with mixtures of carbonic oxide, with hydrogen, or nitrogen only. Experiments are described in which a given volume of hydrogen was added to the volume of gas obtained after some of the carbonic oxide had been absorbed; on completing the absorption, a fresh quantity of carbonic oxide was added, and the experiment repeated. In all cases, whether an ammoniacal or hydrochloric acid solution of cuprous chloride was used, an increase of volume of the hydrogen was observed, the increment being greater in the case of the acid solution. It is advisable, therefore, when carbonic oxide is present in small quantities, to use a fresh ammoniacal solution, or to burn with air by means of palladium asbestos. If the amount of carbonic oxide is large, a portion of the gas is unabsorbed, and must subsequently be determined by the above methods.

V. H. V.

Estimation of Potassium by Reduction of the Platinochloride with Sodium Formate. By WOUSSEN (*Ann. Agronom.*, **13**, 431—432).—The author has made Corenwinder's process workable by securing the agglutination of the reduced platinum. The modified process is conducted as follows:—So much of the substance should be taken as will yield 0.750 to 1 gram of reduced platinum from the potassium platinochloride. This is precipitated with 18 c.c. of a solution of platinum tetrachloride, containing 200 grams per litre, and a slight excess of nitric acid; 8 to 10 c.c. of hydrochloric acid is added, and the solution evaporated to dryness on the water-bath, then taken up with a mixture of nine-tenths alcohol of 96°, and one-tenth ether, filtered, and washed with the same mixture. The mixture of potassium platinochloride and salts remaining on the filter is treated with a jet of boiling water, and the hot solution of the platinochloride thus formed added in portions to a boiling solution of 2 to 2.5 grams of sodium formate in 10 c.c. of water. The boiling is continued for 15 to 20 minutes, and then 8 c.c. of hydrochloric acid is added, and the boiling continued with constant agitation. After this addition the reduced platinum soon agglutinates, and leaves the solution clear; the metal is collected, washed with boiling water, dried, and weighed.

J. M. H. M.

Estimation of Potash in Commercial Manures. By D. LINDO (*Chem. News*, **56**, 163—165).—Gladding has proposed the following method for this purpose:—Boil 10 grams of the manure for 10 minutes with 300 c.c. of water, when cool precipitate by means of a slight excess of ammonia, make up to 500 c.c., and filter. Evaporate 50 c.c. of the filtrate nearly to dryness, add 1 c.c. of dilute sulphuric acid (1 : 1), continue the evaporation to dryness, and ignite. Dissolve the residue in hot water and a few drops of hydrochloric acid, add 5 c.c. of a 2 per cent. solution of sodium chloride and an excess of platinum chloride solution and wash the precipitate successively with alcohol, solution of ammonium chloride (saturated with potassium platinochloride), and finally again with alcohol, dry, &c. The author has made numerous experiments with this method, and finds it simple, more expeditious, and seemingly susceptible of greater accuracy than the methods usually employed.

D. A. L.

Estimation of Sodium Hydroxide in Soda-ash. By R. WILLIAMS (*J. Soc. Chem. Ind.*, **6**, 346).—The following method is found to give accurate results:—A weighed quantity of soda-ash is agitated with strong alcohol in a stoppered flask and left over night; the undissolved carbonate is filtered off and washed with strong alcohol until a drop gives no alkaline reaction; the filtrate and washings are then titrated with normal acid.

D. B.

Estimation of the Relative Amounts of Sodium Hydroxide and Carbonate in Commercial Soda-ash. By P. HART (*J. Soc. Chem. Ind.*, **6**, 347).—The sample under examination is titrated with standard acid, using phenolphthalein as indicator. As soon as the colour disappears, the whole of the hydroxide and one half of the soda

existing as carbonate has been neutralised, the number of c.c. being noted. To the same solution (in which the soda now exists as sodium hydrogen carbonate) a little methyl-orange is added, and the addition of acid from the same burette continued to neutral reaction. By doubling the difference between the two titrations and deducting the number from the number of c.c. consumed, the quantity of hydroxide in the original sample is obtained. D. B.

Analysis of Alum Cakes. By R. WILLIAMS (*Chem. News*, 56, 194—195).—The author has adopted the following methods:—For alumina: neutralise the solution with sodium carbonate, add a large excess of sodium hyposulphite, boil for some time, wash, dry, ignite, and weigh the precipitate. For free sulphuric acid: digest all night with strong alcohol, and titrate the alcoholic extract directly with decinormal soda, using phenolphthaleïn as indicator. Evaporating off the alcohol gives rise to loss, low results are likewise obtained if the digestion is not continued for a sufficient time. In another method, a weighed quantity of quinine, morphine, or strychnine is treated with a known quantity of alum solution, and the alkaloïd reweighed after the treatment, the loss representing the alkaloïd dissolved by the free acid. Comparative results were obtained as follows:—

	Alcohol.	Strychnine.	Quinine.	Morphine.
Free H_2SO_4 per cent...	0.41	0.54	0.50	0.51

The alkaloïd results are all higher than the alcohol, probably on account of some alkaloïd being dissolved by the alum solution and reckoned as sulphate. D. A. L.

Determination of Minute Quantities of Iron, with Special Reference to Alum and Aluminium Sulphate. By R. R. TATLOCK (*J. Soc. Chem. Ind.*, 6, 276—279).—As a standard, a solution of iron-alum is used, of which 1 c.c. equals 0.001 gram iron. Place 1 gram of the finely powdered sample in an ordinary stoppered sample-tube of about 30 c.c. capacity, and having three marks at 7.5, 10, and 20 c.c. respectively. Add 1 c.c. of standard sulphuric acid, and make up to the lowest mark with water. When the alum under examination is dissolved, add 0.2 gram of ammonium thiocyanate and make up to 10 c.c. with water. Place 1 c.c. of the standard iron solution in a 100-c.c. flask, and make up to the latter volume with water. Now place 1 c.c. of this diluted solution in a stoppered sample-tube, add 1 c.c. of standard acid, make up to the lowest mark with water, add 0.2 gram of the thiocyanate, and make up to the 10 c.c. with water. Then fill up both tubes to the 20 c.c. mark with ether, and agitate them thoroughly. As soon as the contents settle, compare the tints, and if unequal make one or more further trials with greater or less quantities of standard iron solution until the two tints correspond. D. B.

Detection and Estimation of Organic Substances. By J. H. SMITH (*J. Soc. Chem. Ind.*, 6, 98—111 and 260—271).—When potassium permanganate is used as an oxidising agent in organic research,

impure products are obtained, and in varying proportions depending on the amount of reagent employed, temperature, and other conditions. It has therefore only been generally employed as a qualitative reagent. From a study of the behaviour of solutions of various organic substances in presence of a large excess of potassium permanganate under varying standard conditions, it occurred to the author that by employing an excess of the reagent, definite and simple compounds would be obtained whose composition in each case might be determined qualitatively by ordinary analysis, and quantitatively by an estimation of the oxygen absorbed in the reaction. The determinations which the author had in view were the following:—Oxygen yielded by excess of manganese dioxide in acid, alkaline and neutral solutions respectively; oxygen yielded by excess of permanganate in such solutions. The latter would include the former, the difference would represent oxygen yielded by permanganate in reduction to manganese dioxide only, and would necessarily correspond with more stable compounds than those represented by the reduction of manganese dioxide. The author further anticipated successive oxidations, more especially of a neutral one succeeded by an alkaline and acid one respectively, and an alkaline oxidation followed by one in acid solution.

It was found, however, that on oxidising an organic or other oxidisable solution by a large excess of permanganate in acid solution, the results generally came out much too high, even for perfect oxidation, which indicated a loss of oxygen due to the presence of manganese dioxide. In order to prevent or diminish the loss, a ferric salt was added to the permanganate solution, the iron acting as an accelerator in the presence of much permanganate and little manganese dioxide, and a retarder when the conditions were reversed. The ferric salt is really an accelerator, but it has the power of neutralising the action of the manganese dioxide after a certain excess has been formed. The accelerating action of iron in presence of much permanganate may be checked by the addition of sodium phosphate to the solution.

The author has based a quantitative method of estimating organic products on the results obtained from this investigation. The method, which is described in detail in the original, is applicable to the estimation of commercial organic substances, the determination of the organic matter in potable waters and in the waste liquors from works employing organic products, whilst for the estimation of alcoholic solutions when largely diluted, it is more rapid than the sp. gr. method.

In the second part of the paper, the author treats of the oxidation of organic substances by means of manganese dioxide in acid solution, as well as of oxidations by permanganate in neutral and alkaline solutions, and of analytical methods derived therefrom. D. B.

The Stalagmometer: a New Method for the Determination of Fusel Oil in Spirituous Liquors. By J. TRAUBE (*Ber.*, 20, 2644—2655).—The author previously described (*Abstr.*, 1886, 743) a method for determining fusel oil in brandy by observing the height of the solution in a capillary tube. In the present paper an apparatus,

called a "stalagmometer," is described by means of which the percentage of fusel oil is determined by counting the drops contained in a known volume of liquid. As in the older method, the brandy is first diluted so as to be about 20 per cent. It is then put into the stalagmometer, and the number of drops from a given volume observed and compared with the number obtained from the same volume of pure 20 per cent. alcohol. An excess of 1.6 drop to 100 c.c. of liquid shows the presence of 0.1 per cent., an excess of 3.5 drops, of 0.2 per cent. of fusel oil. 0.05 per cent. of fusel oil can be determined readily and with certainty.

To increase the delicacy of the method, the proportion of alcohol to fusel oil must be diminished. This is done in the following manner:—300 c.c. of the liquid to be examined (diluted to 20 to 25 per cent.) is shaken in a funnel with 110 to 120 grams of pure ammonium sulphate, and left until two layers are formed; the lower layer, which contains very little fusel oil, is drawn off and shaken with two to three drops of ethyl alcohol or some crystals of ammonium sulphate. In this way the rest of the fusel oil is obtained as a separate layer. These upper layers are now mixed, dissolved in water, and distilled to about two-thirds. The distillate is made up to 110 c.c., the alcohol determined by means of a Westphal's balance, and the number of drops contained in the volume V by means of the stalagmometer. The latter number is compared with that obtained from pure spirit containing a known amount of fusel oil.

A sketch of the apparatus is given, as well as results obtained by means of it. These show that the method is as accurate as that previously described (*loc. cit.*), the new method having the advantage of being more easily worked.

N. H. M.

Assay of Commercial Carbolic Compounds. By J. MUTER and L. DE KONINGH (*Analyst*, 12, 191—195).—*Carbolic Powders.*—Where the phenols exist in the uncombined state, they are extracted by methylated spirit from 75 grams of the powder. Where the powder contains a lime base, a preliminary thorough trituration with a small excess of dilute sulphuric acid is necessary. The alcoholic extract is mixed with 200 c.c. of a 5 per cent. solution of sodium hydroxide, and the mixture is then evaporated to half its bulk. At this point any tar oils and naphthalene will separate and are to be filtered off. The filtrate is further concentrated to 50 c.c. and transferred to a graduated tube. This, which is known as Muter's carbolimeter, is wide in the lower portion. At 65 c.c. it is narrowed to a neck, which is graduated up to 110 c.c. in 0.25 c.c. divisions. It is stoppered, and is furnished with a long, thin, stirring rod, the volume of which must be allowed for. The solution is made up to 65 c.c., 25 c.c. of strong hydrochloric acid are slowly added with stirring, and then enough dry common salt to render the phenols insoluble. The tube is plunged into water of 15.5° and the volume of the phenols read off.

Liquid Carbolic Acid.—If this contains excess of water, it will not give a clear solution with three volumes of benzene. The amount of

water is ascertained by shaking 20 c.c. of the sample with 80 c.c. of a saturated solution of sodium chloride, and observing the diminution in volume. Tar oils are estimated by shaking 20 c.c. with 80 c.c. of soda solution (5 per cent.), and a small quantity of benzene (10 c.c. for dark specimens, less for pale ones). The increase in the volume of the benzene gives the amount of tar oils. The remainder is taken as phenol and cresols.

M. J. S.

Acidimetry with Red Wines. By TONY-GARCIN (*Compt. rend.*, 105, 577).—When red wine, prepared in the ordinary way and not more than a year old is mixed with sodium hydroxide solution, the colour changes to carmine, which becomes deeper and duller and passes into violet-black, which afterwards becomes black, without any tinge of violet, and then changes to green, with formation of a dark, flocculent precipitate. The point at which the colour is brownish-black, without any tinge of violet or green, is the point of exact neutralisation.

C. H. B.

Dairy Products. (*Bull. U. S. Agric. Depart.*, No. 13, 1—128).—*Butter and its Substitutes.*—A series of micro-photographs is given, showing the appearance presented by butter, &c., when examined by polarised light. The black cross described by Hehner and Angell is seen in all the specimens of butter prepared by boiling and slow cooling, and is almost uniformly absent from the crystals obtained from the other fats, nevertheless it is shown by some specimens of butterine and oleomargarine from Armour and Co., Chicago, as well as in a slide prepared from beef suet “oleo oil,” by dissolving in hot alcohol, and cooling slowly, thus confirming the opinion that it is not to be trusted as a characteristic of genuine butter.

The following method for determining the melting point of fats is described:—Thin discs are obtained by dropping the melted fat on to a piece of ice. One of these is placed in a test-tube, the lower part of which contains boiled water, and the upper part strong alcohol. The disc floats between the two liquids. The tube is then warmed in a water-bath, whilst the temperature of the contents is taken by a thermometer with small bulb, situated just above and close to the disc, and kept in motion like a revolving pendulum. The temperature at which the disc contracts to a sphere is taken as the melting point. It is necessary to examine the discs when freshly made, as they show a higher melting point if kept for 24 hours. When the water-alcohol tube is warmed before dropping in the disc, the contraction takes place some 6° lower than when the former method is followed.

Various modifications of Reichert's process are described. Davenport saponifies 5 grams of the butter with only 10 c.c. of alcoholic potash (containing 2 grams of KHO), operating in a flask from which the alcohol vapour is aspirated by a water-pump. Saponification and evaporation to dryness are complete in 15 minutes, and from the statement that genuine butters treated thus require on an average

28·8 c.c. of $\frac{N}{10}$ alkali, there would appear to be no loss of ethyl buty-

rate (compare Allen, Abstr., 1887, 1145). Crampton substitutes phosphoric for sulphuric acid in the distillation, but finds that with care the two give identical results.

Scheffer's test for foreign fats is based on the solvent action of a mixture of amyl alcohol (40 vols.) and ether of sp. gr. 0.715 (60 vols.). 1 gram of butter dissolves in 3 c.c. of this mixture at 28°; 1 gram of lard requires 16 c.c.; 1 gram of stearin 350 c.c.

The following order of value is assigned to the various modes of examining butters for adulteration:—(1.) Determination of volatile acids. (2.) Determination of specific gravity. (3.) Determination of saponification equivalent (Koettstorfer). (4.) Determination of the insoluble acids (Hegner, Muter, Blyth, &c.). (5.) Determination of the melting point.

A complete bibliography of butter analysis (up to 1882) is given by Caldwell (*Second Ann. Rep. N. Y. S. Bd. of Health*, 544—547), and in Sell's *Kunstbutter (Arbeit a. d. Kaiserl. Gesundheitsamte)*.

Milk.—For the determination of water, Babcock employs asbestos to absorb the milk before drying; this is much to be preferred to any powder. By placing the asbestos in a tube between plugs of cotton-wool, and drawing air through the tube while it is heated at 100°, the desiccation is complete in two hours. The tube can then be transferred to the fat extractor.

Of methods for the determination of the fat, the preference is given to that of Adams (Abstr., 1886, 583), but instead of soaking up the milk with one end of the roll of paper, the plan has been adopted of holding the unrolled strip in a horizontal position, and running the 5 c.c. of milk from a pipette along the middle. The strip is then hung up in a hot chamber, and in two or three minutes is dry and ready for rolling up.

In Soxhlet's aræometric method (Abstr., 1881, 656) great difficulty was encountered in ensuring the separation of the ethereal fat solution, and any long delay in the separation was found to affect the final results. By placing the bottles containing the mixture in a centrifugal machine revolving about 300 times per minute, the time required for separation was reduced to a few minutes, only six samples out of 150 requiring more than quarter of an hour. The fat solution thus separated had, however, a lower specific gravity than that obtained by simple subsidence, so that the percentage of fat as given in Soxhlet's table had to be increased by 0.13, to bring it into agreement with the results of the older method. Cronander also separates the fat by shaking the milk with potash and ether, but evaporates the ether after it has risen to the surface of the milk, and measures the fat by forcing it in a melted state into a graduated tube.

Fleischman and Morgen calculate the fat by the formula—

$$f = 0.833t - 2.22 \frac{100S - 100}{S},$$

where f = percentage of fat, t = percentage of total solids, S = specific gravity of the milk at 15°.

Morse and Piggot add 10 c.c. of milk to 20 grams of dehydrated copper sulphate. The milk becomes dry in a few moments. The fat

is then extracted by light petroleum, and its amount determined (after evaporation) by saponification.

Of lactoscopes, Feser's is said to be the most convenient. It is a graduated glass cylinder, containing in its lower part a smaller cylinder of white glass with black lines on it. 4 c.c. of milk are put in the cylinder, and water is added until the black lines become visible. The reading of the total volume gives at once the percentage of fat.

For the determination of the free acid in koumiss, a bright filtrate was obtained by adding to the koumiss an equal volume of alcohol before filtering.

M. J. S.

Extraction of Fats by Soxhlet's Apparatus. By J. M. MILNE (*J. Soc. Chem. Ind.*, 6, 34).—In using the apparatus for milks, the author proceeds as follows:—About 10 c.c. of the milk is weighed into a tared porcelain basin, and the milk evaporated with frequent stirring in order to render it granular, until on being cooled the residue is semi-solid. The residue is then transferred to a paper cup and placed into the Soxhlet tube, and the fat extracted with ether in the usual way. The author having worked with Adams' paper coils for drying up milk for fat extractions, confirms the fact pointed out by the committee of the Society of Public Analysts, that from 0.3 to 0.5 per cent. more fat is extracted by the coil method.

D. B.

Examination of Wines and Oils. By P. SPICA (*Gazzetta*, 17, 304—312).—The author at the outset makes the oft-repeated complaint that the conditions, such as the variation of concentration, or even the nature of the acids used, required for the successful application of test-reactions, are not defined with sufficient exactness in original papers. Various processes have been proposed to recognise the colouring matters, whether natural or artificial, of wines; but preference is given by the author to the methods proposed by Caze-neuve (Abstr., 1886, 397), Arata (*Gazzetta*, 17, 44), Blarez and Deniges (Abstr., 1886, 1084), and Girard and Gautier. In the last-named process the substitution of tablets of *Magnesia alba* for those of plaster of Paris is suggested; these are immersed in egg albumin for a short time and dried. A drop of the wine to be examined is let fall on such a prepared tablet, and the colour of the stain produced is observed. The natural colouring matters of wine give a yellowish-brown, those containing rosaniline or "vinoline" a reddish-yellow, those with indigo an azure-green, with orchil a violet red, and those with amaranth a greyish-violet stain. Another method suggested consists in shaking up the wine with baryta-water and amyl alcohol, when the latter extracts the colouring matter from the wine. It appears that certain preparations containing coal-tar colouring matters, called "vinoline," are sold by druggists in Padua. An examination of such a preparation, called "maroon vinoline," was found to consist of about 40 per cent. of mineral matter, in which arsenic was present in considerable quantities.

As regards the method of examination of oils proposed by Maumené, which is founded on the rise of temperature when the

sample is mixed with concentrated sulphuric acid, it appears that a confusion has arisen between grams and cubic centimetres. Concordant results are obtained with mixtures of 50 grams or 55 c.c. of oil with 10 c.c. of acid.

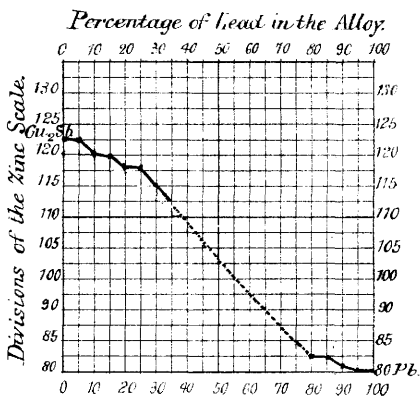
Bechi has proposed a method for the recognition of cotton-seed oil in olive oil, which consists in adding to the oil an alcoholic-etheral solution of silver nitrate in presence of an amyl alcohol solution of petroleum; it is here shown that this method gives fallacious results. A method of the greatest practical value is that proposed by Hubl, which has given satisfactory results in the hands of Moore, Allen, Ogialoro, and other observers.

V. H. V.

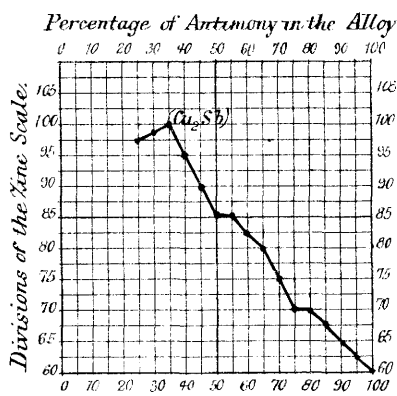
Gravimetric Estimation of Tannins. By H. R. PROCTER (*J. Soc. Chem. Ind.*, 6, 94—96).—The process described by the author is a combination of the methods published by Müntz and Simand, and depends on the fact that in filtration through a column of dry hide powder the upper layers absorb most of the tannin, a very complete and rapid separation being obtained from the large surface exposed. The author utilises the lamp chimneys employed in the common round-wicked German petroleum lamps, which are contracted just above the base of the flame and are cylindrical for the remainder of their length. A perforated disc of cork is made slightly cup-shaped on its two faces. A piece of linen is then stretched over it, and it is pressed down the chimney until it rests on the contracted neck. Five grams of hide powder is weighed into the tube, and when shaken down will occupy a space of about 50 c.c. The tube is now cut off, allowing only length for the insertion of a cork, which may press slightly on the powder, as it contracts in volume when wet. This cork is perforated and hollowed like the first, and after being covered with linen is pressed into the tube. A short piece of quill tubing passes through the cork, and is fitted by a second cork into a flask. The filtering tube is inverted, broad end downwards, into a beaker of 100 c.c. capacity, which is filled with the liquid to be filtered until it rises into the hide powder. The tube is left in this position for one or two hours, after which it is reversed, and the enlarged end filled with the solution, when the filtration will be found to proceed evenly and steadily. The filtrates thus obtained are perfectly free from tannin, and tested by the Löwenthal method show a lower result for "non-tannin" than those by any other method of absorption. The method is, however, inapplicable in the presence of gallic acid, the latter being freely absorbed by hide powder. The author hopes to overcome the difficulty either by some method of removing the gallic acid or of preventing its absorption by the hide.

D. B.

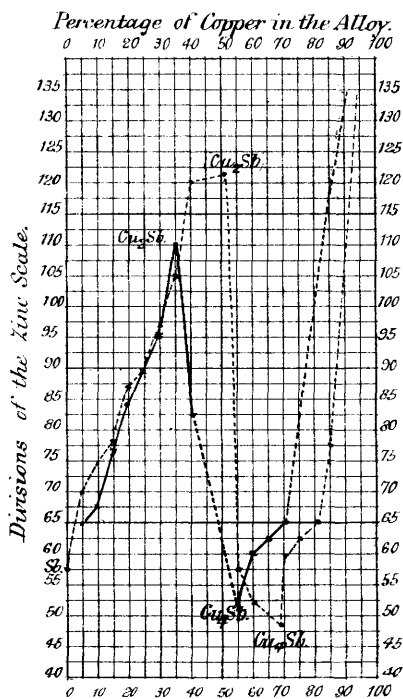
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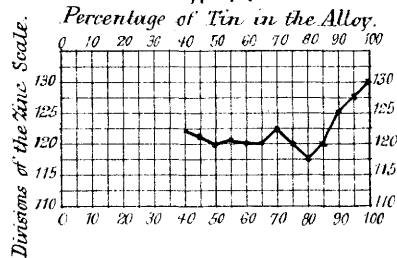
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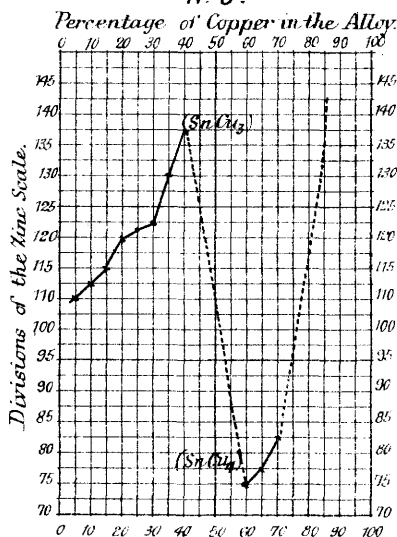
N^o 3.



N^o 4.



N^o 5.



General and Physical Chemistry.

Relation between the Composition and Absorption-spectra of Organic Dyes. By H. W. VOGEL (*Ber. Akad. Ber.*, 1887, 715—718).—Experiments made with azo-dyes gave the following results:—The substitution of methyl for hydrogen in diazobenzene gives rise to change of position of the absorption-bands towards the red end of the spectrum. The increase of wave-length is 10 millionths mm. when the substitution takes place in the ortho-position, and 14 millionths mm. in the case of the para-position. (2.) The substitution of β -naphtholsulphonic acid S or β -naphtholdisulphonic acid R for β -naphtholsulphonic acid B, causes a shifting of the bands which, in the case of β -naphtholsulphonic acid S amounts to 4 to 5 millionths mm., and in the case of β -naphtholdisulphonic acid R to 6 millionths mm. (3.) In the substitution of methyl, the space between the two bands becomes clearer, and the bands become more equal in intensity and in width. The substitution of β -naphtholsulphonic acid S or β -naphtholdisulphonic acid R, in the place of the acid B, acts similarly on the character of the bands.

The above results were obtained with sulphuric acid solutions; the results, as well as those obtained with alcoholic solutions, are shown in tables. N. H. M.

Fluorescences with Well-defined Spectra. By L. DE BOIS-BAUDRAN (*Compt. rend.*, 105, 784—788).—When gallium oxide is employed as a solid solvent of other oxides, it gives fluorescences which are usually much less brilliant than those obtained with alumina, but the results are of the same order. Calcination of the oxide at a very high temperature converts the bands in the spectrum into lines, the spectral groups being displaced towards the red. The brilliancy of the spectrum increases with the time of action of the electric discharge, a result contrary to that obtained with alumina.

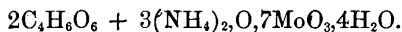
Measurements are given of the spectra of the fluorescences of gallium oxide with oxides of samarium, $Z\alpha$ and $Z\beta$. The fluorescence of $Z\beta$ with gallium oxide is very feeble, the difference between $Z\alpha$ and $Z\beta$ being even more strongly marked than when the oxides are mixed with alumina.

A moderately calcined mixture of alumina with praseodymium oxide yields only a very faint trace of a rosy fluorescence, but if the mixture is very strongly heated, it then yields a beautiful fluorescence, the colour of which depends on the time during which the electric discharge has been passing. At first it is violet, but afterwards becomes rose-coloured. The spectrum is complicated, the principal bands, all of which are nebulous, being situated at 6457, 6237, 6162, 6035, and 5212. C. H. B.

Rotatory Power of Solutions of Ammonium Molybdate and Tartaric Acid. By D. GERNEZ (*Compt. rend.*, 105, 803—806).—
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The experiments previously made with solutions of tartaric acid and sodium molybdate (Abstr., 1887, 540) were repeated with ammonium molybdate. The rotatory power increases regularly as the quantity of ammonium molybdate increases, and is proportional to the quantity of this salt present up to a quarter of an equivalent. Between one-fourth and one-third of an equivalent, the increase of rotation for the same weight of molybdate changes suddenly, and becomes little more than half its original value. The maximum rotation observed is 57 times that of tartaric acid, and corresponds with a proportion of ammonium molybdate equal to one-third of an equivalent, it remains sensibly constant between $42\cdot66/128$ and $56/128$ of an equivalent of molybdate. With large quantities, the rotatory power diminishes rapidly, and becomes practically constant when one equivalent of molybdate is present.

As in the case of sodium molybdate, the tartaric acid at first combines with the whole of the ammonium molybdate, forming a compound of the composition $8C_4H_6O_6 + 3(NH_4)_2O, 7MoO_3, 4H_2O$, which is gradually converted into a second compound, containing 6 mols. of tartaric acid and 1 mol. of the molybdate, and this is finally transformed into a third more stable compound,



In the case of sodium molybdate, the maximum rotation is obtained with one equivalent of the salt, whilst in the case of the ammonium molybdate, the maximum rotation is given by one-third of an equivalent. The ammonium salt, however, contains three equivalents of the alkali in the molecule for each equivalent present in the molecule of the sodium salt, and hence in each case the maximum rotation is given by compounds which contain the alkali and the tartaric acid in equal equivalents.

C. H. B.

Influence of Light on the Heat Conductivity of Selenium. By M. BELLATI and S. LUSSANA (*Gazzetta*, 17, 391—405).—The analogies of heat and electric conductivity induced the authors to study the influence of light on the heat conductivity of selenium, the electric resistance of which, as is well known, is diminished on exposure. The plan of experiment consisted in sprinkling the double iodide of copper and mercury on the disc of selenium, on which a circular figure had been blackened with Indian ink. The selenium was heated by the passage of an electric current, which produced at first a dark spot, owing to the change in colour of the double iodide. This subsequently extended into a fairly regular circular figure, the measurement of the diameter of which afforded a means of determining the heat conductivity of the selenium. This method was found to be more practicable than the usual method of melting wax. In all cases, the diameter of the circle was greater when the selenium was exposed to reflected sunlight from which the greater part of the heat rays had been removed by passage through solutions of alum and of ammoniacal copper sulphate. The relation of heat conductivity without and with exposure to light was found to be in the ratio of 1:1.1 as the result of several concordant experiments. The same

ratio was observed between the electric conductivities without and with exposure to light under conditions similar to those described above. The authors, however, would not insist on this concordance of results in the two phenomena.

V. H. V.

Effect of Light on the Conductivity of Selenium. By S. KALISCHER (*Ann. Phys. Chem.* [2], 32, 108).—Of the selenium cells constructed by the author, three in which copper and copper-brass electrodes are used, are found to differ from the rest in their behaviour on exposure to light, the resistance rapidly increasing after undergoing a momentary decrease, and the cell only returning to its normal condition on remaining for some time in the dark. The conclusion drawn from this is, that the cells in question contain a hitherto unknown modification of selenium, the conductivity of which decreases instead of increasing under the action of light. As the author's other cells which do not exhibit the peculiarity described, differ from the above in having zinc, copper-zinc, and copper-platinum electrodes, it still remains to be ascertained whether the nature of the electrodes has any influence on this behaviour of selenium. The phenomenon in question has also been observed and described by Hesehus (*Exn. Rep. d. Phys.*, 20, 490).

H. C.

New Galvanic Battery. By F. FRIEDRICH (Ann. Phys. Chem. [2], 32, 191).—A tube running below the cells of this battery connects each with a common reservoir, by the raising or lowering of which the fluid used can be transmitted to or removed from the cells. A tap attached at the end of the tube opposite the reservoir allows the fluid to be removed when exhausted. An advantage claimed over other batteries is, that spontaneous evaporation of the liquid and consequent crystallisation of salts when the battery is not in use, is avoided.

H. C.

Galvanic Polarisation. By F. STRENTZ (*Ann. Phys. Chem.* [2], 32, 116).—The author has examined the galvanic polarisation produced on aluminium and silver plates. The results for aluminium have been already given (*Abstr.*, 1887, 415). With silver, the oxygen plate is found to attain maximum polarisation when the E.M.F. of the cell used is equal to that of three Daniells; the polarisation of the hydrogen plates is at a maximum when an E.M.F. of two Daniells is used, it decreases when a greater E.M.F. is employed, but rises again and becomes equal to the first maximum for an E.M.F. of nine Daniells. The explanation given is that the deposition of metallic silver on the cathode, which is greater the greater the intensity of the current, by increasing the surface decreases the relative strength of the current and amount of the polarisation, so that although a small E.M.F. produces maximum polarisation with clean plates, a very considerable one is required to attain the same maximum with plates thickly coated with silver.

H. C.

Production of Electricity by the Condensation of Aqueous Vapour. By L. PALMIERI (*Nuovo Cimento* [3], 22, 34—39).—The occasion of this paper is the confirmation by Firmin Larroque (*La*

Lumière Élect., 1887) of the author's experiments on the production of electricity by the condensation of aqueous vapour. On the other hand, the experiments of Kalischer (*Abstr.*, 1884, 138) led to negative results, but Tait considers that these were conducted on far too small a scale. Accordingly the author has repeated on a large scale his experiments on the condensation of aqueous vapour on a beaker of platinum containing ice, and connected with a condensing electric cup; in all cases, the production of electricity was observed. The author remarks that his observations, extending over 37 years, leave no doubt in his mind as to the production of electricity under these conditions. The potential of atmospheric electricity is conditioned by the state of the weather; the author's observations also have more particularly shown that the potential is affected by the eruptions at Vesuvius.

V. H. V.

Electrolysis of Water. By H. v. HELMHOLTZ (*Ber. Akad. Ber.*, 1887, 749—757).—Previous experiments made by the author showed that the smaller the amount of dissolved hydrogen and oxygen near the electrodes, the smaller the electromotive force necessary to electrolyse water. The experiments described in the present paper were made with a view to determine the limits for the smallest electromotive force capable of producing fresh gas under a given pressure of the oxyhydrogen mixture on the liquid. In previous experiments, an error in the measurement of the electromotive force of the decomposition of water was caused by hydrogen or other combustible gas being occluded in the platinum anode or in both electrodes, so that the oxygen carried over in the current comes in contact with the gases of the anodes, and thus bubbles of hydrogen will be liberated at the cathodes with a much less expenditure of electromotive force. To avoid this, the current is kept in the same direction for weeks or months. An apparatus is described with sketch, by means of which the gases produced by the electrolysis are removed as soon as formed, and a vacuum is thus kept above the liquid; the flask containing the solution is so inclined that a small bubble of gas is retained; the gas under these conditions occupies a space 1000 times greater than it would under normal pressure, and the diameter of the bubble is measured in order to ascertain whether it remains the same size or whether it increases.

To produce a current, three carbon-iron ferric chloride solution elements were used; the electromotive force was diminished daily in order to determine the limit. The limit for the evolution of gas was found to be 1.64 to 1.63 volt, with a pressure of oxyhydrogen gas = 10 mm. of water.

The influence of pressure on electromotive force is expressed as follows:—

$$A = A_0 + 10^{-7} \cdot \eta \cdot \theta \left\{ R_h \frac{2\alpha_h}{2\alpha_h + \alpha_0} \log \left(\frac{p_h}{p_a} \right) + R_0 \cdot \frac{\alpha_0}{2\alpha_h + \alpha_0} \log \left(\frac{p_0}{p_a} \right) \right\}.$$

p_a = atmospheric pressure, p_h and p_0 are the pressures of hydrogen

and of oxygen above the liquid; α_h and α_o are the atomic weights of the two elements; θ is the absolute temperature.

$$R_h = \frac{p_h \cdot v_h}{\theta} = 41461000 \cdot \frac{cm^2 \cdot g}{sc^2},$$

where v_h is the volume of 1 gram of hydrogen; R_o the corresponding constant for oxygen, and η the amount of water decomposed in a second by one Ampère. $\eta = 0.00009319$ according to Kohlrausch.

When pure oxyhydrogen gas is above the liquid, as in the experiments described, $p = p_h + p_o$, the part of the electromotive force changing with the pressure becomes—

$$A_1 - A_2 = \frac{1}{6} \cdot 10^{-7} \cdot \eta \cdot \theta \cdot R_h \cdot \log \left(\frac{p_1}{p_2} \right) = 0.018868 \cdot \log \text{nat.} \left(\frac{p_1}{p_2} \right).$$

N. H. M.

Electrolytic Separation of the Metal on the Free Surface of the Solution of its Salt. By J. GUBKIN (*Ann. Phys. Chem.* [2], **32**, 114).—When an electric current passes from a solution of a salt into the atmosphere of gas or vapour immediately above it, an electrolytic separation of the metal takes place at the surface of the liquid. Apparatus is described by means of which this is made evident, the space above the liquid being either vacuum or exposed to the air in the ordinary way. Silver and platinum are found to separate out in films which float on the surface; zinc oxidises as it separates out, the white flakes of zinc oxide gradually falling to the bottom.

H. C.

Action of the Solvent on Electrolytic Conduction. By T. C. FITZPATRICK (*Phil. Mag.* [5], **24**, 377—391).—The author continues his researches on the conductivity of salt solutions, the solvents being varied. The salts examined were calcium, lithium, and magnesium chlorides and nitrates, and ferric and mercuric chlorides, the solvents being water and ethyl and methyl alcohols. Tables of conductivities are given. With mercuric chloride, which is the only salt more soluble in alcohol than in water, the conductivities are little more than those of the solvents alone. For aqueous solutions, the chlorides conduct better than the nitrates; magnesium chloride is anomalous, its conductivity being half that of calcium chloride. Ferric chloride in dilute solution shows signs of dissociation. With alcoholic solutions, the conductivity is not proportional to the amount in solution. The conductivity of lithium salts in ethyl alcohol is 10 to 20 times as great as that of the other salts. In all cases, the aqueous solutions conduct better than the alcoholic ones, the character of the solvent appearing to have an influence on the conductivity. This the author considers to be due to the formation of molecular groups in the solutions. He finds that the conductivity of salt solutions at low temperatures points to the existence in solution of cryohydrates at temperatures above their solidifying points, and also that the conductivity of mixed solvents and of salts in mixed solvents differs from the calculated values, showing that an interaction has taken place with formation of new molecular groups. The action then of the

solvent is twofold: (1) decomposition of the salt, the amount depending on the temperature, nature of solvent, and state of dilution; (2) the formation of fresh molecular groups in the solution.

H. K. T.

Influence of a Magnetic Field on the Thermoelectric Properties of Bismuth. By G. P. GRIMALDI (*Nuovo Cimento* [3], **21**, 57).—It is well known that a magnetic field influences in a remarkable degree the electric resistance of bismuth; in this paper, the author shows that its thermoelectric force when paired with copper is varied in a similar degree. This pile was placed in the field of an electromagnet, and coupled up with a galvanometer, in which readings were taken without and with a current passing round the electromagnet. After due allowance for induction, it is shown that the thermoelectric force of the bismuth-copper pair is materially decreased in the magnetic field. The experimental enquiry is, however, only in the preliminary stage.

V. H. V.

Rotation of Isothermic Lines of Bismuth placed in a Magnetic Field. By A. RIGHI (*Gazzetta*, **17**, 359).—In the course of experiments on the heat conductivity of bismuth when placed in a magnetic field, it was observed that the isothermic lines were rotated in a direction opposite to that of the magnetising current when a rectangular strip of the metal was placed with its planes normal to the line of force. The phenomenon is analogous to that observed by Hall, namely, the rotation of the equipotential lines when a magnet acts on a current flowing along a thin strip of metal, and may explain the thermomagnetic currents recently discovered by Ettingshausen.

V. H. V.

Thermic Conductivity of Bismuth in a Magnetic Field. By A. RIGHI (*Gazzetta*, **17**, 358—359).—The author, as well as other physicists, has observed the marked variation of the electric conductivity of bismuth when placed in a magnetic field (Abstr., 1887, 109), and the production of Hall's phenomenon under these conditions. Considering the correlation of electric and thermic conductivity, the effect of magnetic field was also studied; the results of the experiments showed that with a field of 4570 C.G.S. units the thermic conductivity of bismuth is to that of the metal under ordinary conditions as 1 : 0·886. This result must at present be only considered as approximate; further experiments are being made with more refined apparatus.

V. H. V.

Specific Heat of Superfused Water. By P. CARDANI and F. TOMASINI (*Nuovo Cimento* [3], **21**, 185).—The specific heat of water at various temperatures has been the subject of numerous investigations, although the results obtained are far from concordant. Thus at temperatures 0—10°, Hirn, as also Pfandler and Platter, has observed a marked increase of specific heat, whilst Rowland on the other hand observed a decrease. In this paper, a description is given of experiments made to determine the specific heat of water in the superfused condition. The method adopted in the investigation is practically an application of the weight thermometer; a known

volume of water is enclosed by mercury within a bulb, connected with which is a capillary tube bent twice at right angles. The whole apparatus is completely filled with water and mercury, and the bulb cooled by suitable freezing mixtures, then the mercury driven out by the expanding water is collected and weighed. The apparatus is then agitated, and the mercury driven out by the solidification of the water is also collected and weighed. Then from these data, together with a determination of the temperature at the moment of solidification, and the quantity of heat absorbed by the glass and the mercury contained, the specific heat of the water at the temperature of solidification is ascertained. The various experimental errors are discussed in full, and the data of all the observations given in a series of tables. The following are the main conclusions: the specific heat of super-fused water is less than unity; it increases with decrease of temperature from a minimum at a temperature of -6.52° to 0° . The final results are given below.

Temperature.	Specific heat.
-6.52° to 0°	0.953
-8.09 „ 0	0.961
-9.47 „ 0	0.962
-10.67 „ 0	0.985

V. H. V.

New Form of Calorimeter. By W. F. BARRETT (*Proc. R. Dublin Soc.*, 5, 13—16).—The instrument devised by the author is a modification of Bunsen's calorimeter. The cup for holding the substance under experiment forms part of a mercurial thermometer. The cup has a capacity of 4 c.c., and is surrounded by a jacket of polished metal. The stem of the thermometer, of which the cup is a portion, is supported horizontally, and graduated from -5° to 80° . Supported immediately above the cup is a small burette, the level of the liquid in which can be accurately read. The neck of the burette may be closed by a short thermometer graduated from 30° to 100° . In making a determination of the specific heat of a liquid with this instrument, the weight of the liquid must be found by taking its specific gravity for the temperature at which it was used; the volume of the liquid used having been read from the burette. This inconvenience may be obviated by converting the thermometer into a balance, the stem being supported by knife-edges somewhere near its centre of gravity. From the end of the stem, a pan is suspended, and beyond this a pointer, fixed to the stem, moves over a graduated arc. With a calorimeter balanced in this way, the weight of the liquid at a given air-temperature may be found directly.

B. H. B.

Determining the Specific Gravity of Small Quantities of Dense or Porous Substances. By J. JOLY (*Proc. R. Dublin Soc.*, 5, 41—47).—The method generally employed for determining the specific gravity of small quantities of minerals of low density is by balancing in a liquid of known specific gravity. This method, however, is inapplicable when the substance has a specific gravity over 4, and also when the substance is of a porous nature. Under these conditions, the

substance may be mixed with another substance of much lower specific gravity in such proportion that the specific gravity of the mixed substances may be as close to that of either of them as may be desired. For this purpose, the author uses the paraffin sold in the form of candles. The transparency of the paraffin enables the appearance of the embedded mineral to be minutely examined. Results are given showing the accuracy of the method. B. H. B.

Dissociation of Copper Sulphate. By W. MÜLLER-ERZBACH (*Ann. Phys. Chem.* [2], 32, 313).—The author has studied the dissociation of copper sulphate at higher temperatures than those which he previously employed, and finds that his results agree with those obtained by Lescœur (Abstr., 1887, 208). The paper also contains a discussion of the dependence of chemical affinity on temperature (Abstr., 1887, 628). With sodium phosphate containing 5 mols. H_2O , and sulphuric acid of 1.294 sp. gr., water passes from the acid to the salt at 32° , but the change is reversed, and water passes from the salt to the acid at 47° . The equilibrium between the affinity of copper sulphate and of dilute sulphuric acid for water occurs, as might be expected, at higher temperatures the more dilute the acid.

H. C.

Rate of Dissociation as a Measure of the Vapour-tension of Hydrated Salts. By R. SCHULZE (*Ann. Phys. Chem.* [2], 32, 329).—A reply to Müller-Erzbach. The author seeks to justify his former conclusions with regard to Müller-Erzbach's method of determining the vapour-tension of hydrated salts (Abstr., 1887, 766). Müller-Erzbach having objected to the use of zinc sulphate as being a salt which admittedly exhibits irregularities in its behaviour, copper sulphate is here shown to act in an irregular manner also when investigated by the above method. In two out of three tubes containing copper sulphate, evaporation set in at 20° , but the third did not exhibit any change even at the end of 10 weeks.

H. C.

Interaction of Metals and Sulphuric Acid. By V. H. VELEY (*Chem. News*, 56, 221—222).—In this communication, the author points out that the results obtained by Spring and Aubin in their investigation on the action of acids on zinc containing lead (Abstr., 1887, 1074) do not adequately represent the rate of chemical change as comparable, for example, with the rate of evolution of a gas from a homogeneous liquid. Thus the initial retardation or "induction" observed may be due to the adherence of bubbles of gas to the surface of the metal, and, secondly, when the change has set in, the metal is surrounded by a concentrated solution of the metallic salt, which is only in part removed by the gas bubbles. The hydrogen evolved is a resultant of a series of changes, each one of which is variable at any moment, such as the rate of diffusion of the salt of the metal in the acid liquid, the amount of surface exposed (which Spring and Aubin in some experiments kept approximately constant), and the local rise of temperature. The amount of gases other than hydrogen, such as sulphurous anhydride and hydrogen sulphide, is doubtless also dependent on the more or less perfect removal of the products of the

change from the sphere of the dissolving metal as well as on the concentration of the acid solution. On the other hand, it does not seem that variations in the relative masses of zinc could make any difference either in the rate of solution or in the products of the change, provided that the surfaces exposed were equal. The dissolution of a solid in a liquid must be regarded as a superficial action only. The author is at present studying the rate of solution of metals in acid liquids under such conditions that not only fresh surfaces of a regular geometrical figure are continuously being exposed, but also the products of the change, whether gas or metallic salt, are at once and continuously removed from the vicinity of the dissolving metal.

V. H. V.

Velocity of the Formation of Ethereal Salts. By N. MEN-SCHUTKIN (*Compt. rend.*, 105, 1016—1019).—The particular reaction investigated was the action of acetic anhydride on alcohols, $\text{Ac}_2\text{O} + \text{RHO} = \text{AcOR} + \text{AcOH}$, at 100° . With most alcohols, the reaction is complete. The formation of the ethereal salt is accompanied by a change of volume, which is least with methyl alcohol and increasingly greater with ethyl, propyl, and isobutyl alcohols. In order to eliminate this variable, the mixture of acetic anhydride and alcohol was diluted with 15 volumes of benzene. The constants of velocity are calculated from the equation $\frac{dx}{dt} = C(A - x)(B - x)$, in which A and B are the quantities of the substances originally present, and x the quantity of the new substance formed in time t . A and B being equal, and x and t being 0, $\frac{x}{A - x} = CA t$, which gives the constant C. The results given in the following tables are the mean of several concordant experiments, the constants of velocity being referred to that observed with methyl alcohol, which is taken as 100:—

Primary alcohols.	Constants of velocity.	
Methyl alcohol	0·1053	100·0
Ethyl „	0·0505	47·9
Propyl „	0·0480	45·6
Butyl „	0·0465	44·1
Isobutyl „	0·0401	38·1
Heptyl „ (normal)	0·0393	37·3
Octyl „ „	0·0377	35·8
Tetradecyl alcohol (normal).	0·0291	27·6
Hexadecyl „ „	0·0269	25·5
Octodecyl „ „	0·0245	23·2
Melissyl „ „	0·0174	16·5
Allyl „ „	0·0287	27·2
α -Methyl allyl alcohol	0·0267	25·3
Benzyl alcohol	0·0280	26·6

Secondary alcohols.	Constants of velocity.	
Isopropyl alcohol	0·0148	14·1
Methyl ethyl carbinol	0·0123	11·6
Methyl hexyl „	0·00916	8·7
Methyl allyl „	0·00643	6·1
Tertiary alcohol.		
Trimethyl carbinol	0·00091	0·8

The ethereal salts of the tertiary alcohols, phenols, and propargyl alcohol are decomposed by acetic acid, and hence in these cases the reactions are not comparable with those of primary alcohols.

The greatest velocity is observed with methyl alcohol. The velocity is affected by the isomerism of the radicles in the alcohols, but is highest with primary alcohols, and much lower with secondary alcohols, whilst in the case of tertiary alcohols it is very small indeed. In homologous alcohols of analogous constitution, the constant of velocity diminishes as the molecular weight increases, the difference being greatest in the normal primary alcohols. Non-saturated alcohols have a lower constant of velocity than the corresponding saturated alcohols.

C. H. B.

Inorganic Chemistry.

Action of Carbon Bisulphide on Metals. By A. CAVAZZI (*Chem. Centr.*, 1887, 888, from *Mem. R. Acc. Sc. Inst. Bologna* [4], 7, 27–33).—Carbon bisulphide vapour when passed over the heavy metals in a fine state of division and heated to a high temperature yields metallic sulphides with separation of carbon in a graphitoidal form. Other compounds of carbon with sulphur seem not to be formed in any case. V. H. V.

Formation of Hydrates of Lithium Hydroxide from Alcoholic Solutions: Quantitative Determination of Lithium. By C. GÖTTIG (*Ber.*, 20, 2912–2915).—Lithium hydroxide generally separates from hot saturated solutions in 96·8 per cent. alcohol with $\frac{1}{2}$ mol. H_2O ; when in contact with water, it shows the movements previously observed with crystals of potassium and sodium hydroxide (*Abstr.*, 1887, 636).

When lithium hydroxide is crystallised from 62·8 per cent. alcohol, a hydrate with 1 mol. H_2O is obtained; the crystals do not move when placed in contact with water.

In determining lithium as sulphate, the sulphate must be ignited for a long time until of constant weight. N. H. M.

Transformation of Ammonium Nitrate. By M. BELLATI and R. ROMANESE (*Nuovo Cimento* [3], 21, 5–24).—Frankenheim, and, more recently, Lehmann have shown that ammonium nitrate crystallises in various forms, according to the temperature at which the

crystallisation is effected. Thus at 36° it crystallises in the trimetric system, at 87° in the rhombohedral, and at 120° in the monometric system. In the present paper, it is shown that at these various points the salt undergoes other physical modifications. Thus, on warming, the temperature of the salt increases in direct proportion to the time up to a temperature of 35.67° ; so also the rate of cooling is regular up to 30.3° , reaching a minimum at 30.07° ; it then increases to 31.05° , at which point it remains constant for some time. Similar phenomena are also observable at a temperature of 85.5° to 86.5° with ascending temperature, and 82.2° to 82.6° with descending temperature, as also at 124.8° and 124.05° .

The variations of volume corresponding with these crystalline changes is also determined in an accurately calibrated dilatometer containing oil of turpentine, a liquid whose expansion is regular, and which, when properly dried, does not dissolve the salt. Results show that the curve of coefficient of expansion has two points of inflection: one at a temperature between 33.29° and 41.29° , and another at about 85° ; the formula expressing the rate of expansion from 0° to the former of these points is $v_1 = v_0 (1 + 0.000339t + 0.000000346t^2)$, whilst between 40° and 85° this becomes $v_1 = v_0 (1.04957 + 0.00038756t + 0.000008976t^2 + 0.0000000432t^3)$. There is also an alteration in the value of the mean specific heat at the temperature of these crystalline transformations; applying the method of mixtures and using oil of turpentine as the liquid, it is shown that the mean specific heat from 0 — 31° is 0.407 , from 31° to 82.5° is 0.355 , and from 82.5° to 124° is 0.426 . Hence the following values are deduced for the heats of transformation at these points:—

$$\begin{aligned}\text{At } 31.0^\circ &= 5.02 \\ \text{,, } 82.5 &= 5.33 \\ \text{,, } 124.0 &= 11.86\end{aligned}$$

The values obtained for the specific heats of ammonium nitrate are compared with those of Kopp and Tillinger, and the methods of correction applied by the latter are criticised. V. H. V.

Ammonium Phosphites. By L. AMAT (*Compt. rend.*, 105, 809—811).—A solution of phosphorous acid mixed with ammonia until neutral to methyl-orange, and then concentrated until the weight of the liquid is one-fourth or one-fifth more than the calculated weight of the salt, yields large, deliquescent crystals which can be dried over sulphuric acid or at 100° . Similar crystals are obtained if the liquid is concentrated in a vacuum at the ordinary temperature. The crystals have the composition $\text{NH}_4\cdot\text{H}_2\text{PO}_3$, and seem to be monoclinic prisms; they melt at 123° and are very soluble in water. At 145° they lose half their ammonia without evolution of hydrogen phosphide, and yield a gummy mass which seems to contain crystals. At a higher temperature, ammonia and hydrogen phosphide are given off and phosphoric acid is formed.

Hydrated diammonium phosphite, $(\text{NH}_4)_2\text{HPO}_3 + 2\text{H}_2\text{O}$, when kept in a dry vacuum at the ordinary temperature or heated at 100° , loses water and ammonia, and yields the monammonium salt just

described. Both at the ordinary temperature and at 100° , the water is given off before the ammonia.

Monammonium phosphite has no appreciable action on ammonia gas at the ordinary temperature, but at 80° to 100° absorption is rapid, and the anhydrous diammonium salt is obtained as a white powder. The corresponding compounds of sodium and potassium have not yet been obtained. C. H. B.

Effects produced by Small Quantities of Bismuth on the Ductility of Silver. By J. SCULLY (*Chem. News*, 56, 224—226; 232—244; 247—248).—It is observed that the Indian method of wet assay is incidentally a delicate test for bismuth in presence of a large excess of silver. The bullion is dissolved in nitric acid, the solution diluted, excess of hydrochloric acid added, and the whole vigorously agitated to facilitate the aggregation of the silver chloride, which settles down and generally leaves a clear supernatant liquid; if, however, the liquid is turbid and the silver chloride on exposure to light, while still under the liquid, remains white, the turbidity is due to mercury, if on the other hand, the silver chloride becomes discoloured, the turbidity is due to bismuth; tin and antimony having been proved to be absent when dissolving in nitric acid. In such cases, to prevent the vitiation of the silver assay, the following modified method has proved successful:—The assay pound of bullion is dissolved in 5.5 c.c. of nitric acid, sp. gr. 1.200, the solution is mixed with 5 ozs. of water and 10 c.c. of nitric acid, sp. gr. 1.320, then 2.5 c.c. of hydrochloric acid are added, and the method proceeds as usual. For the estimation of the bismuth, having obtained a rough idea of the amount of bismuth present from the amount of turbidity in the trial assay, sufficient bullion to yield a weighable amount of bismuth is dissolved in a small quantity of nitric acid, the solution diluted and heated with excess of ammonium carbonate, which dissolves the silver and copper carbonates, but leaves the bismuth carbonate insoluble; the latter is then washed, dried, ignited, and weighed. If lead or cadmium are present they would remain with the bismuth carbonate; the latter, however, is not likely to be present, and the former may be separated by dissolving the bismuth carbonate in nitric acid, and evaporating down with sulphuric acid; the lead sulphate is treated in the usual manner and weighed, whilst the bismuth is reconverted into carbonate and estimated as described above.

Fine silver, or silver containing 10 per 1000 of copper, alloyed with 1 to 5 per 1000 of bismuth and cooled rapidly, had its ductility, as tested by rolling, sensibly but slightly impaired, the straps having jagged edges; with 6 per 1000 of bismuth, the decrease in ductility was more evident, whilst fine silver with 9 to 11 per 1000 of bismuth was so brittle as to break with a mere tap. When, however, the cooling was gradual, 4 per 1000 of bismuth was sufficient to make the silver or silver-copper alloy mentioned above highly brittle, the fracture being crystalline in the case of fine silver and granular in the silver-copper alloy. With Indian standard silver containing 83.4 per 1000 of copper, 2 per 1000 of bismuth produced red shortness and jagged straps: as the quantity of bismuth increased the evidence of diminished

ductility is more decisive, and with 10 per 1000 of bismuth the alloy was very brittle and had a granular fracture; the mode of cooling had no appreciable effect on the ductility of these alloys. Other experiments with Indian coinage bars show that the ductility of bullion is not materially affected by the presence of 0.5 per 1000 of bismuth.

As the refining fine silver containing bismuth is both tedious and attended with loss of silver, the author suggests dilution with silver free from bismuth as a practical means of overcoming the brittleness. The author remarks on the concordance of his results with those of Gowland and Koga (*Trans.*, 1887, 410—416), as regards the question of brittleness. The discrepancy in reference to refining bismuth silver he suggests is possibly due to the Japanese silver containing more base metals than the Indian silver; it consequently supplied more slagging material and greater facilities for refining.

D. A. I.

Combination of Silver Chloride with Metallic Chlorides.

By M. C. LEA (*Amer. J. Sci.*, **34**, 384—387).—If hydrochloric acid is mixed first with ferric chloride and then with silver nitrate, the silver chloride which forms is not white but buff-coloured. The ferric chloride cannot be removed by washing, and is only partially removed by treatment with hydrochloric acid. The presence of the minute quantity of ferric chloride makes the silver chloride remarkably less sensitive to light.

Cobalt chloride and hydrochloric acid give a silver chloride which is pink and contains cobalt; but the reduction in the sensitiveness to light is very much less than when iron is present. Nickel and manganese behave similarly, but cupric chloride seems to have no tendency to combine with silver chloride. The tendency of gold chloride to combine with the silver chloride is, however, well marked, and the precipitate has a reddish shade, but the influence on the sensitiveness is not easily determined, since the gold is rapidly reduced to the metallic state, and the silver chloride darkens to black instead of to chocolate or violet as would be the case if it were pure.

In analytical determinations, it is important to digest the silver chloride for a considerable time with hydrochloric acid, and even then it is doubtful if the foreign chloride is entirely removed, especially if it is ferric chloride.

These observations show that silver chloride has a great tendency to combine with small quantities of other chlorides, and supports the author's view as to the nature of the "photo-salts" (this vol., p. 1). They also explain the fact that a small quantity of mercuric chloride very greatly reduces the sensitiveness of silver chloride to light. In order to ascertain the presence of mercury in the silver chloride, the author employs a solution of stannous chloride in hydrochloric acid which has no action on silver chloride if light is carefully excluded, but gives a brown or brownish-black colour to the precipitate if mercury is present. The author was unable to remove mercuric chloride from silver chloride even by very prolonged washing.

Poitevin's observation that his coloured photographic images resisted the action of light better after they were treated with dextrin and

lead chloride is explained by the tendency of the lead salt to prevent alteration of silver chloride.

C. H. B.

Silver Potassium Carbonate. By A. DE SCHULTEN (*Compt. rend.*, 105, 811—813).—When silver carbonate is formed by the action of an alkaline carbonate on silver nitrate, the precipitate is sometimes white, sometimes yellow, but always becomes yellow when washed. If silver nitrate is added to an excess of a concentrated solution of potassium carbonate containing some hydrogen carbonate, a white precipitate is formed which changes to microscopic crystals of the composition AgKCO_3 . This compound is decomposed by water, with removal of the potassium carbonate and formation of yellow silver carbonate.

150 grams of potassium carbonate is dissolved in 150 c.c. of water, cooled and agitated with 15 grams of potassium hydrogen carbonate. When the liquid is saturated with the latter salt at the ordinary temperature, it is filtered and mixed with a solution of 1 gram of silver nitrate in 25 c.c. of water. In order to obtain large crystals, the liquid containing the precipitate is heated with continual agitation. The precipitate dissolves, and when the liquid is cooled it deposits long, transparent crystals with a brilliant lustre; sp. gr. 3.769. They do not blacken when exposed to light except in the presence of organic matter, and when treated with water, the silver carbonate which remains retains the form of the original crystals. When heated, the compound loses carbonic anhydride, and at a higher temperature the silver oxide which is formed gives off oxygen.

The crystals are microscopic, rectangular lamellæ with a terminal angle closely approaching 90° . The refraction is almost identical with that of apatite; the extinction of parallel polarised light takes place longitudinally; twinning plane parallel with the plane of the optical axes; sign of elongation positive; maximum birefractive power approximately 0.0216.

C. H. B.

Lead Aluminium Sulphate. By G. H. BAILEY (*J. Soc. Chem. Ind.*, 6, 415).—The author has examined some crystals which have been noticed in a mordanting liquor (aluminium nitroacetate) prepared by dissolving up alum, lead acetate, and lead nitrate in water and allowing to settle. The crystals form octahedra crystallising in cruciform aggregates like alum. They are, however, not transparent and are quite unaltered by exposure to air. The substance is a lead alum, $\text{Pb}_2\text{Al}_2(\text{SO}_4)_3 + 20\text{H}_2\text{O}$, formed under special conditions of concentration and temperature.

D. B.

New Oxide of Thallium. By A. PICCINI (*Gazzetta*, 17, 450—452).—Carstanjen has observed that when a rapid current of chlorine is passed through a concentrated solution of potash in which thallium sesquioxide is suspended, the solution acquires a violet colour which is considered to be due to a potassium thallate. The same liquid is also formed when thallium hydroxide is submitted to electrolysis, using a plate of thallium as an electrode, as also on adding potassium hypochlorite to a quarter of its weight of caustic potash to which thallium sulphate is subsequently added. On digesting the whole and adding barium nitrate, a violet precipitate is finally obtained. The results of

analyses made to determine the relation between thallium and barium in this precipitate led to discordant results, but sufficient evidence was afforded to point to a formula, TlO_2 , for the oxide of thallium. The isolation of this oxide brings out a further point of analogy of the thallium compounds to those of lead. Experiments made to prepare the corresponding sulphur compound have not as yet been successful, although substances have been obtained which contain a proportion of sulphur greater than that required for the trisulphide.

V. H. V.

Constitution of Basic Salts. By S. U. PICKERING (*Chem. News*, 56, 210—212).—In the author's opinion, those basic compounds, which although seemingly of indefinite composition can scarcely be regarded as mere mixtures, are precisely analogous to the complex hydrates, which he contends constitute a solution of a salt in water. Hydrated basic salts of copper may be obtained of a composition corresponding with that of an anhydrous salt of the formula $17\text{CuO}, \text{SO}_3$, but the most basic definite sulphate known is $4\text{CuO}, \text{SO}_3$, therefore if these higher basic salts are to be regarded as mixtures, they must be mixtures of a basic salt with copper hydroxide and not mixtures of two different basic salts.

To investigate this point, a series of basic copper salts were prepared by diluting a solution of ammonio-copper sulphate with increasing quantities of water; the precipitates were dried in a vacuum, and analysed. The results, although not decisive, tend to show that free copper hydroxide is not present in these compounds, for on comparing any two preparations of different basicity, the excess of copper oxide present in the more basic one is not accompanied by a constant proportion of water.

D. A. L.

Crystallised Mercurous Iodide and Bromide. By A. STROMAN (*Ber.*, 20, 2818—2823).—If a saturated solution of mercurous nitrate, as free as possible from oxide and slightly acidified with nitric acid, is heated to boiling with iodine, the latter becomes covered with a yellow powder, which partially dissolves, and the solution, after decantation into a warm dish, deposits, in the dark, lustrous, yellow, transparent, tetragonal scales of mercurous iodide; these must be dried in the dark at the ordinary temperature. When the mercurous nitrate solution is treated with an alcoholic solution of iodine in the cold, small, yellow spangles of mercurous iodide are obtained, but the product formed by the old methods of preparation, that is, by rubbing together molecular proportions of mercury and iodine, and by adding potassium iodide in solution to a solution of a mercurous salt, have a green colour, and are impure, although the pure yellow compound can be obtained by reversing the last process and adding an excess of a dilute solution of mercurous nitrate to potassium iodide in solution. The crystallised compound shows the same colour-change as observed by Yvon (this Journal, 1873, 1105), but the change does not begin at 60° , as stated by him, since the salt is still a pure yellow at 100° , and only passes from this colour through dark yellow and orange to garnet-red at higher temperatures. Sublimation commences at 110 — 120° , not at 190° as stated by Yvon, and the

salt fuses at 290° with decomposition. Towards acids and solvents, the crystallised compound behaves like that precipitated by potassium iodide; ammonia and caustic alkalis render it green, and on heating convert it into the corresponding alkaline iodide and metallic mercury. The crystallised iodide is less sensitive to light than the precipitated yellow compound, which rapidly becomes black even in diffused daylight.

When mercurous nitrate solution is treated with bromine under similar conditions, small, white, nacreous, tetragonal scales of mercurous bromide are obtained, and the same compound separates in yellow, crystalline spangles when an alcoholic or aqueous solution of bromine is employed. It sublimates at $340\text{--}350^{\circ}$ in small scales, is less sensitive to light than the iodide, dissolves in hot sulphuric acid with the evolution of sulphurous anhydride, becomes black and gradually decomposes when heated with dilute and concentrated hydrochloric acid, dissolves slowly in hot nitric acid (sp. gr. = 1.42), and decomposes with the formation of the corresponding bromides when treated with ammonia and caustic alkalis.

W. P. W.

Atomic Weight of Yttrium Metals in their Natural Compounds: Gadolinite. By C. RAMMELSBERG (*Ber. Akad. Ber.*, 1887, 549—556).—According to Nordenskiöld (*Abstr.*, 1887, 109), the oxides of the yttrium metals occur in their natural compounds in proportions so nearly constant that he suggests the term gadolinium oxide for this mixture of yttrium, erbium, and ytterbium oxides.

The author shows from the results of 29 analyses of minerals from different sources and by various chemists, that this mixed oxide, so far from being constant, would give atomic weights varying from 97.5—132.5° for the mixture of metals.

Analyses of gadolinite from Hitterö and Ytterby gave the following results:—

	Hitterö.	Ytterby.
Silica	24.36	25.53
Yttrium earths.....	45.51	38.13
Cerium oxide.....	7.01	13.55
Ferric oxide	2.85	4.07
Ferrous oxide	11.50	7.47
Beryllium oxide	8.58	10.03
Lime	0.36	0.57
Loss on ignition	0.50	1.34
	<hr/> 100.67	<hr/> 100.51

N. H. M.

Water of Crystallisation of Alums. By J. JUTTKE (*Chem. Centr.*, 18, 777).—Potash alum, in a vacuum over sulphuric acid, loses 19 mols. H_2O , chromium alum 12—13, and iron alum, 20—21 mols. H_2O . Potash alum, heated at 100° in a current of dry air, loses 15 mols. H_2O readily, but the remainder only after prolonged heating, and breaking up of the dry crust, which retains the water. At a temperature of $20\text{--}30^{\circ}$ potash alum gives off no water, at 42° 11 mols., at $65\text{--}91^{\circ}$ 19 mols., and at 100° the remaining 5 mols. of water are

given off. Potassium, chromium, and ammonium iron alum heated at 100° are completely dehydrated, without becoming insoluble in water, and without undergoing any decomposition. V. H. V.

Action of Hydrogen Sulphide on Cobalt Salts. By H. BAUBIGNY (*Compt. rend.*, 105, 751—754, and 806—809).—The action of hydrogen sulphide on solutions of cobalt salts varies, as in the case of nickel salts (*Abstr.*, 1882, 1031), with the concentration of the solution, the nature of the acid in the salt, the ratio between the weight of acid and metal present, the ratio of free acid to the water present, the degree of saturation with hydrogen sulphide, or in other words the tension of the gas, and also with certain other conditions, including the temperature and the duration of the experiment.

Solutions of the normal sulphates of cobalt and nickel were saturated with hydrogen sulphide, and hermetically sealed in glass flasks, the liquid occupying about five-sixths of the volume of the flask. After standing for some days, precipitation is always more complete in the case of nickel than with cobalt. This, however, is only a special result. Under comparable conditions the formation of cobalt sulphide from a solution of a cobalt salt is always more rapid than the formation of nickel sulphide from the corresponding nickel salt. This is observed, for example, if the solutions saturated with hydrogen sulphide only partially fill the vessels. It follows that the tension of the gas exercises a considerable influence on the result.

Precipitation of the cobalt sulphide is prevented by the presence of free acetic acid, the proportion required to produce this result being greater the greater the concentration of the solution. More acetic acid is necessary to prevent the precipitation of cobalt than to prevent that of nickel. With sulphuric acid and similar acids, however, the differences between the two metals tend to disappear. In both cases, there is no precipitation even after several days at the ordinary temperature if the proportion of free sulphuric acid is equal to half that in combination with the metal, provided that the quantity of salt present exceeds 0.15 gram per litre. If the solutions are more dilute, some precipitation takes place, the quantity of sulphide formed being greater in the case of cobalt than in the case of nickel. The presence of the precipitated sulphide accelerates the reaction in both cases.

Rise of temperature accelerates precipitation from solutions of cobalt sulphate, but precipitation is not as complete as with nickel sulphate under the same conditions. The precipitation of nickel in fact takes place more readily than the precipitation of cobalt as the acidity of the solution increases. The more concentrated the original solution of the neutral salt, and consequently the greater the quantity of acid liberated during the reaction, the greater is the precipitation of the nickel as compared with that of cobalt. It follows that a smaller quantity of free acid is required to prevent the precipitation of cobalt than to prevent that of nickel. With weak acids, the difference is still distinct. In a solution containing only a small proportion of free acetic acid, the precipitation is greater in the case of cobalt, but if the proportion of free acid is increased the precipitation of nickel becomes the greater of the two.

C. H. B.

Action of Vanadic Anhydride on Potassium Fluoride. By A. DITTE (*Compt. rend.*, 105, 1067—1070).—When excess of vanadic anhydride is fused with potassium fluoride in a platinum crucible, care being taken to prevent access of air, a brick-red, crystalline mass is formed on cooling, and when this is treated with water, a residue of vanadic anhydride is left, and a red solution is obtained. The solution first deposits a small quantity of potassium bivanadate, formed in consequence of access of air, and then orange-red plates of the compound $3V_2O_5, 2KF + 5H_2O$, which melts easily to a black liquid. The mother-liquor on further concentration deposits red, transparent prisms of the composition $4V_2O_5, 2KF + 8H_2O$.

Contact with air is more completely avoided by heating the crucible at the bottom of a long glass tube. Under these conditions the aqueous solution first deposits the compound $3V_2O_5, 2KF + 5H_2O$, then ruby-red prisms of the composition $3V_2O_5, 2KF + 6H_2O$, and less soluble, lemon-yellow crystals of the composition $3V_2O_5, 4KF$.

All these compounds are soluble in concentrated sulphuric acid, with evolution of hydrogen fluoride and formation of a red solution which becomes pale-green when diluted with much water.

When an excess of potassium fluoride is employed, the residue is pale-yellow, and on treatment with cold water first yields a saturated solution of potassium fluoride, in which the vanadium compounds are practically insoluble. A further quantity of water forms a yellow solution, which deposits small plates of the composition $2V_2O_5, 2KF + 8H_2O$, and the mother-liquor when concentrated in a vacuum yields the compound $3V_2O_5, 2KF + 4H_2O$. The portion of the residue least soluble in water has the composition $V_2O_5, 4KF + 3H_2O$.

With a large excess of potassium fluoride, the solution yields successively large, thin, brilliant, orange-yellow lamellæ of the compound $3V_2O_5, 2KF + 5H_2O$, white crystals with a greenish-yellow tinge of the compound $V_2O_5, 8KF + 3H_2O$, and finally yellow crystals of the compound $V_2O_5, 4KF + 2H_2O$.

If air has free access and vanadic anhydride is in excess, the residue is an orange-red mass with a vitreous fracture, and when treated with hot water some vanadic anhydride remains undissolved. The solution first deposits potassium bivanadate, and afterwards lemon-yellow crystals of the composition $V_2O_5, 4KF$. Similar results are obtained with excess of potassium fluoride. Water first dissolves the excess of fluoride, and the solution obtained by further treatment deposits yellowish-white crystals of the compound $V_2O_5, 8KF + 2H_2O$.

The action of potassium fluoride on vanadic anhydride yields the compounds $2V_2O_5, KF$; $3V_2O_5, 2KF$; V_2O_5, KF ; $3V_2O_5, 4KF$; $V_2O_5, 4KF$; $V_2O_5, 8KF$, which may be regarded as analogous to potassium chlorochromate. Their solutions give no coloration and no precipitate with ammonia. If these compounds are regarded as derived from an oxy-fluoride, the latter must be $V_2O_4F_2$. Possibly the compounds do not actually exist in the fused mass, but the aqueous solution contains several different compounds, giving rise to conditions of equilibrium in which the crystallisable salts described are formed. A solution of potassium fluoride dissolves vanadic anhydride, and the liquid deposits

greenish-white crystals of the compound $V_2O_5, 8KF$, which is but slightly soluble in excess of the alkaline fluoride. As the colourless solution cools it becomes yellow, and deposits lemon-yellow crystals of the compound $V_2O_5, 4KF$.

C. H. B.

Mineralogical Chemistry.

Metamorphic Graphite: Strata containing Garnet from the Ural Mountains. By A. KARPINSKY (*Chem. Centr.*, 1887, 821—822; from *Bull. Akad. St. Petersb.*, **31**, 484—495).—On the banks of the Bagarjak, on the eastern side of the Ural Mountains, a peculiar instance occurs of strata of graphite in limestone, thus indicating a remarkable nonconformability of the strata of the carboniferous period. In the limestone are found crinoides, in the sandstone are crystals of hornblende and quartz, together with orthoclase and plagioclase, whilst in the neighbouring village of Fadina are the usual fossils of the carboniferous period, such as stigmaria and lepidodendron. The presence of small specimens of garnet in the graphite containing strata of limestone is peculiar. An analysis of specimens gave the following results:—

SiO ₂ .	Al ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Sp. gr.
37·12	21·31	8·82	25·83	5·72	0·94	4·065

from which the formula $3\text{Mn}_3\text{Si}_3\text{O}_{12}(\text{Cu}, \text{Mg})_3\text{Al}_2\text{Si}_3\text{O}_{12}, \text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ is deduced. The crystals were formed from twelve rhombic faces, whose apices converge in the centre of the crystal, and whose bases were of rhombic form.

V. H. V.

Mineral Wax. By G. DOLLFUS and S. MEUNIER (*Compt. rend.*, **105**, 823—824).—The mineral was obtained from Sloboda Rungorska, near Kolomea, in Austrian Galicia. It occurs in petroliferous strata formed of compact non-aqueous and non-fossiliferous bluish-grey marls. It has a fibrous structure with a golden-yellow lustre, some samples strongly resembling crocidolite, whilst others resemble colophony. It melts at above 80°; sp. gr. 0·6. Boiling water does not dissolve it, and does not remove any chlorides. When placed in ether, it first becomes white and then dissolves, and if the solution is concentrated, it deposits long, colourless, monoclinic needles, which act strongly on polarised light. It imparts a yellow colour to carbon bisulphide, which gradually dissolves a considerable quantity. It is less soluble in alcohol, from which it crystallises in nacreous, white plates. The mineral has the composition C_nH_n , distils without residue, and burns with a very luminous flame.

C. H. B.

Artificial Deposition of Calcite Crystals on Spicules of a Sponge. By W. J. SOLLAS (*Proc. R. Dublin Soc.*, **5**, 73).—After

having been left to stand for some days in water containing an excess of calcium carbonate, some acerate and triradiate spicules of a calcisponge were found to have become incrustated with crystals of calcite. The optic axes of the calcite forming a spicule, and the crystals deposited on it, are similarly orientated. The crystals are deposited only on those regions which show the greatest liability to solution (compare Sollas, *ibid.*, 4, 385). B. H. B.

Howlite. By S. L. PENFIELD and E. S. SPERRY (*Amer. J. Sci.*, 34, 220—222).—The specimen examined was obtained from the gypsum quarries at Windsor, Nova Scotia. It consisted of an egg-shaped nodule, one inch and a half in diameter, composed of microscopic flattened prisms usually broken at the ends, but occasionally terminated by two dome faces. Analysis of the air-dry powder gave the following results:—

SiO ₂ .	B ₂ O ₃ .	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	SO ₃ .	Total.
14·70	42·69	28·20	0·51	0·12	11·97	2·01	100·20

The mineral is thus a very acid silico-borate, having the formula $H_5Ca_2B_5SiO_{14}$. In the above analysis the boric anhydride was determined by the method suggested by F. A. Gooch (*Abstr.*, 1887, 299), a method that was found to give most satisfactory results.

B. H. B.

Celestine and Anglesite by Senarmont's Process. By L. BOURGEOIS (*Compt. rend.*, 105, 1072—1074).—Amorphous strontium and lead sulphates heated in sealed tubes at 150° with hydrochloric acid diluted with twice its volume of water are converted into crystals of celestine and anglesite respectively. Strontium sulphate is heated with an excess of acid. Lead sulphate on the other hand is employed in large excess, and the lead chloride which is formed is removed by treatment first with cold and then with boiling water.

C. H. B.

Mursinskite. By N. v. KOKSCHAROFF (*Chem. Centr.*, 1887, 817, from *Bull. Acad. St. Petersb.*, 31, 450—464).—This new mineral forms inclusions in topaz and is extremely scarce, sufficient material not yet having been obtained for an analysis, although it was first noticed 32 years ago. It crystallises in the tetragonal system in forms derived from a tetragonal pyramid; axial ratios $a : b : b = 0·56641 : 1 : 1$; colour wine to honey-yellow; hardness 5—6; sp. gr. = 4·149 (?). A. J. G.

Occurrence of Harmotome in Wicklow. By J. JOLY (*Proc. R. Dublin Soc.*, 5, 165—168).—The mineral described occurs implanted on a quartz matrix in the Lunganure lode, which traverses the granite of Glendalough in Co. Wicklow. The results of measurements of the crystals are in accord with those recorded by Dana, although the appearance of the crystals differs from that usually assigned to harmotome, one set of the prism faces being reduced to minute dimensions. The sp. gr. of the mineral is 2·46, and its hardness is 4·5. Before the blowpipe, it fuses without intumescence. It

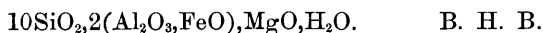
does not gelatinise with, but is decomposed by, hydrochloric acid. These tests confirm its identity with harmotome. No occurrence of any zeolite in Wicklow has hitherto been recorded. B. H. B.

Beryl and Iolite of Glencullen. By J. JOLY (*Proc. R. Dublin Soc.*, 5, 48—72).—The minerals described occur in the granite of Glencullen, Co. Dublin. The beryl crystals occur in veins and bunches, and present three types: normal crystals, radiating crystals, and altered crystals. The normal beryl is of a pale apple-green colour, semitransparent to translucent. It has a sp. gr. of 2·722. Interpenetration by orthoclase is common in these crystals. The second type is remarkable in habit. The crystals radiate in a striking manner, the groups being all more or less fan-like in section. It was found by experiment that a temperature of 357° is sufficient to decolorise both green and yellow beryls in a very short time, whether in contact with air or not. With long-continued heating the temperature of alteration is possibly below 250°. The greater proportion of the total number of beryl crystals coming from Glencullen belong to the third type. The author's observations show that these crystals were primarily composed entirely of beryl, subjected to reaction with a potash felspar in a state of hot solution. They were partially replaced, the result being a variable mixture of felspar and beryl, pseudomorphous after beryl. The felspar thus mixed with the beryl is orthoclase containing iolite, a mineral as a rule foreign to Irish rocks.

The minute crystals developed through the felspar, and absent from the portions of the sections composed of beryl, appear in two forms: a wide polygonal form and a rectangular elongated form. The crystals are transparent, with uncertain dichroism. They have a pale blue colour, a vitreous lustre, a sp. gr. of 2·56, and a hardness of about 7. The fusibility is about that of iolite. On fusion, the mineral loses transparency. These characteristics clearly indicate that the small crystals are iolite. Analysis of an impure specimen gave the following results:—

SiO ₂ .	Al ₂ O ₃ .	FeO.	MgO.	CaO.	MnO.	H ₂ O.	Total.
56·7	20·7	13·9	4·2	trace.	trace.	2·0	97·5

The formula deduced from this imperfect analysis is—



Studies in the Mica-group. By F W. CLARKE (*Amer. J. Sci.*, 34, 131—137).—1. *Muscovite from Alexander Co., North Carolina.*—This mica (Analysis I) occurs at Stony Point with dolomite, iron pyrites, and rutile. All these minerals are dusted over with a dark-green chloritic coating (Analysis II), which appears to be a member of the obscure hisingerite group. A microscopical examination of the mica showed that the angle of the optic axes, measured in oil in a plane perpendicular to the plane of symmetry, is 35°.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MgO.	Na ₂ O.	K ₂ O.	F.	Ignition.	Total.
I.	45·40	1·10	33·66	2·36	1·86	1·41	8·33	0·69	5·46	100·27
II.	31·16	—	8·06	35·86	5·43	—	—	—	20·50	101·01

2. *Lepidomelane from Baltimore and Maine*.—These minerals gave on analysis the following results:—

	H ₂ O.	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.
III.	4.48	35.78	16.39	14.55	11.02	1.08	—
IV.	4.67	32.35	17.47	24.22	13.11	1.02	0.89

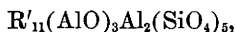
	MgO.	K ₂ O.	Na ₂ O.	Total.
III.	8.67	7.76	0.56	100.29
IV.	—	0.70	6.40	100.83

III. Baltimore; formula $R'_6R''_3R'''_4Si_5O_{22}$. IV. Litchfield, Maine; formula $R'_6R''_2R'''_6Si_5O_{24}$.

These two micas and the so-called annite of Rockport (Abstr., 1887, 347), which has the formula $R'_6R''_4R'''_2Si_5O_{20}$, are built up on the same fundamental plan, and exhibit a new and highly suggestive order of variation. All the monoxide bases being united, the following general formulæ are obtained:—

Rochport.....	$R'_{14}R''_{12}(SiO_4)_5$.
Baltimore.....	$R'_{12}(AlO)_2R''_2(SiO_4)_5$.
Litchfield.....	$R'_{10}(AlO)_4R'''_2(SiO_4)_5$.

3. *Iron-biotite from Auburn, Maine*.—In its ratios, this mica is not simple. Its formula may be approximately written—



with $R'_{11} = H_4K_2Fe_{21}$. It seems to be a compound intermediate between the Litchfield and Baltimore micas, with R''' nearly all aluminium.

4. *Iron-mica from near Pike's Peak*.—This specimen was a bronzy-black mica, the entire core of which was made up of a soft rotten material evidently derived from the original mica. Analyses of the broad black margin of mica (V) and of the centre (VI) gave the following results:—

	H ₂ O.	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.
V.	4.54	34.21	16.53	20.15	14.17	0.91	0.48	1.34
VI.	7.82	34.63	17.95	31.25	3.01	0.34	0.81	1.08

	Na ₂ O.	K ₂ O.	F.	Total.
V.	1.43	6.50	0.08	100.34
VI.	0.89	1.96	0.54	100.28

B. H. B.

Crocidolite from Cumberland, Rhode Island. By A. H. CHESTER and F. I. CAIRNS (*Amer. J. Sci.*, **34**, 108—111).—At Beacon Pole Hill, near the well-known mineral locality, Diamond Hill, Cumberland, Rhode Island, crocidolite occurs usually disseminated in fine particles through felspar, but often in larger, radiated nodules. Its colour is usually a dark, bluish-grey. Analysis gave the following results:—

	SiO ₂ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	Na ₂ O.	H ₂ O.	Total.
I. 52.13	15.93	21.25	—	0.22	6.26	3.95	99.74	
II. 51.03	17.88	21.19	—	0.09	6.41	3.64	100.24*	
III. 52.11	20.26	16.51	0.75	1.88	5.79	3.53	100.83	

I and II crocidolite from Cumberland: sp. gr. 3.2; III is a new analysis of crocidolite from the Orange River, South Africa. The empirical formula suggested for crocidolite is $\text{Fe}_3\text{Na}_2\text{H}_4\text{Fe}_2\text{Si}_9\text{O}_{27}$, or $3\text{FeO}, \text{Na}_2\text{O}, 2\text{H}_2\text{O}, \text{Fe}_2\text{O}_3, 9\text{SiO}_2$. The authors regard crocidolite as one of the well-authenticated mineral species, and cannot agree with the conclusions of Dölter and of Kenngott (Abstr., 1886, 128), that crocidolite is merely a fibrous variety of arfvedsonite.

The mineral, named *abriachanite* by Heddle (*Min. Mag.*, 3, 61), and the crocidolite from the Vosges Mountains, analysed by Delesse, are shown to be essentially the same substance—a magnesian variety of crocidolite. B. H. B.

Nature and Formation of Glauconite. By C. W. v. GUMBEL (*Chem. Centr.*, 1887, 813—814, from *Ber. Münch. Akad.*, 1886, 418—449).—The author has examined specimens of glauconite from different geological formations, and established their identity; specimens of this mineral from the coast of New Jersey are more particularly examined, analysis of which gave the following results:—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.
46.9	4.06	27.09	3.6	0.2	0.7	6.16	1.28	9.25

There were present, in addition, traces of organic substances, manganese, phosphoric acid, and sulphuric acid. The author combats the view of Ehrenberg as to the suspected connection between the remnants of foraminiferæ and glauconite: it seems more probable that glauconite has been intussuscepted between the shells of the foraminiferæ. The condition of formation was probably a shallow sea, in the muddy deposits of which organisms were included, and in their decomposition gave off hydrocarbons, carbonic acid, and hydrogen sulphide. At the surface of the bubbles of gas mineral substances—such as lime, silicic acid, and, in some cases, glauconite separated, which subsequently increased by intussusception. In the ferriferous earths of Kressenberg, the nuclei of brown oxide, which is probably a metamorphic product of glauconite, has penetrated into the shells of conchylæ and echinodermata. V. H. V.

Black Marble of Kilkenny. By W. N. HARTLEY (*Proc. R. Dublin Soc.*, 5, 486—488).—At the quarries from which this well-known marble is procured, the author noticed that the weathered surfaces of the rock exhibit a yellow-ochreous colour. This might be caused by the colour of the freshly-hewn marble being due to the presence of ferrous sulphide or of ferrous carbonate which, in presence of carbonic acid and air, become dissolved and oxidised. Fractured surfaces smelt of hydrogen sulphide, due to the existence of calcium hydro-

* This total is given as 99.94 in the original.

sulphide in the rock. Analysis of the marble gave the following results:—

CO ₂ .	CaO.	FeO.	CuO.	MgO.	SiO ₂ .	H ₂ O.	C.	S.	Total.
40.41	55.36	0.34	0.05	0.24	1.44	0.60	1.48	0.01	99.93
B. H. B.									

Analyses of Calcareous Rocks and Pozzuolana from Tevere.

By VERRI and TROTTARELLI (*Gazzetta*, 17, 385—390).—In this paper, a series of analyses are set forth of calcareous rocks from the Tevere basin; typical specimens from the several geological periods are selected. References are also given to former memoirs in the *Reale Accademia dei Lincei* and the *Bull. Soc. Geol.*

Amongst others the following analyses of pozzuolana are of particular interest:—

	Moisture.	Organic matter.	SiO ₂ .	CaO.
Red pozzuolana	3.38	4.4	44.03	2.8
Grey pozzuolana from Attighano.	2.3	3.33	59.60	2.11
Grey pozzuolana from Orte.....	1.66	2.087	54.37	6.63
Maroon pozzuolana from Larni ..	7.5	4.7	46.7	3.31

	Al ₂ O ₃ .	Fe ₂ O ₃ .	MgO.	K ₂ O or Na ₂ O.
Red pozzuolana	30.31	9.61	1.82	3.46
Grey pozzuolana from Attighano.	30.3	6.7	0.775	3.69
Grey pozzuolana from Orte.....	6.04	24.56	0.16	1.63
Maroon pozzuolana from Larni...	13.61	20.57	9.23	3.26

V. H. V.

Serpentine of the Onondaga Salt-group at Syracuse. By G. H. WILLIAMS (*Amer. J. Sci.*, 34, 137—145).—The eruptive nature of the matrix of the serpentine (peridotite) of Syracuse, New York, is proved from its structure, and from the inclusion of fragments of the adjacent limestone, in opposition to T. S. Hunt's theory of the aqueous origin of serpentine. Pyrope and ilmenite were not detected in the Syracuse serpentine. Chrome-iron ore and perovskite, however, are present, as was shown by an analysis of 0.0165 gram of the filtrate obtained by digesting the finely-powdered rock for a long time in concentrated hydrochloric acid under pressure, and by treating the residue with strong sulphuric acid. The analysis gave—

TiO ₂ .	CaO.	FeO.	Total.
34.54	12.12	54.54	101.20

B. H. B.

Peperite of the Puy de la Piquette. By F. GONNARD (*Compt. rend.*, 105, 886—888).—The “Wacke” of the Puy de la Piquette was described by Lecoq and Bouillet as a bluish peperite of sp. gr. 2·2 to 2·3, which effervesces with an acid, and melts before the blow-pipe to a brownish-black enamel. It contains fragments of basalt, highly cellular black scoria, small crystals of hornblende, calcareous nodules and crystals of mesotype, with masses of carbonised wood, the latter being covered with fibrolamellar crystals of mesotype. The calcareous nodules enclose mesotype in crystals and crystalline masses.

Apophyllite in nacreous, white, partially translucent crystals of the form $m(110)$, $p(001)$, $a'(101)$, also occurs in the calcareous nodules, but not in the peperite itself. It occurs in small druses, and also associated with mesotype in radiating bundles, the character of which shows that the apophyllite is a later formation than the mesotype. Analcime is also present in the peperite, but not in the calcareous nodules. There are also small crystals of felspar round which, in many cases, the analcime has accumulated, and crystals of green diallage accompanied by mica. C. H. B.

An Iron of doubtful Origin. By R. B. RIGGS (*Amer. J. Sci.*, 34, 60).—This iron was found on a farm in Jefferson County, Tennessee, in a region full of small iron furnaces, whence have come a number of pseudo-meteorites. The iron is characterised by extreme hardness; its weight is 640 grams, and its sp. gr. 7·61. Analysis gave the following results:—

Fe.	Ni.	Co.	Cu.	As.	Mn.	Mg.	P.
88·27	0·76	0·19	0·03	trace	6·73	0·14	1·80
	Si.	Graphite.	C.	Total.			
	0·15	0·86	1·46	100·39			

Treated with nitric acid, the polished surfaces developed fine markings not unlike Widmanstätten figures. B. H. B.

New Meteoric Iron. By R. B. RIGGS (*Amer. J. Sci.*, 34, 59).—This meteorite was found in a collection of minerals made by the late Colonel J. J. Abert. It weighed 456 grams, and in cross-section measured 50 by 37 mm. Analysis gave the following results:—

Fe.	Ni.	Co.	P.	S.	Graphite.	C.	Total.	Sp. gr.
92·04	7·00	0·68	0·08	0·01	0·03	0·02	99·86	7·89

In composition, therefore, it is similar to the Nelson County meteorite. B. H. B.

Aërolite from Rensselaer Co., New York. By S. C. H. BAILEY (*Amer. J. Sci.*, 34, 60—62).—In 1863 a stone of unusual appearance was found on the bank of the Tomhannock Creek in Rensselaer Co. In 1884 it was recognised as an aërolite. It weighed 1·5 kilos., with an average diameter of 10 cm. In its general aspect, upon a cut

surface, it resembles the Seres, Macedonia stone. For many years this aërolite seems to have been exposed to the action of the atmosphere and of the soil without showing any deterioration. An analysis of the metallic portion of the stone gave 13·02 per cent. of metallic iron, and 3·06 per cent. of nickel. The composition of the stony portion has not yet been determined. B. H. B.

Deposition of Scorodite from Arsenical Waters in the Yellowstone Park. By A. HAGUE (*Amer. J. Sci.*, **34**, 171—175).—Scorodite, although a comparatively rare mineral, is found at a number of localities in the Yellowstone Park as an incrustation deposited from the water of hot springs and geysers. The best occurrence is at the Joseph's Coat Springs on Broad Creek, east of the Grand Cañon, in the form a brilliant green deposit upon the sinter. Frequently the cavities in the sinter are filled with scorodite, and occasionally it forms nodular masses half an inch in diameter. Analysis (I) of the mineral shows a nearly pure scorodite.

Other localities are Chrome Springs, and one or two places in Norris Basin. At the Constant Geyser in Norris Basin, a specimen of scorodite was analysed (II); it contained a large quantity of silica. Scorodite, as deposited from these thermal waters, is evidently a very unstable mineral. It slowly undergoes oxidation, leaving an ochreous material containing varying amounts of arsenic acid.

	Analysis III.		Analysis IV.	
	Grams per kilogram of water.	Per cent. of total material in solution.	Grams per kilogram.	Per cent. of total material in solution.
SiO ₂	0·4685	28·88	0·3828	27·52
SO ₃	0·0923	5·69	0·0152	1·09
CO ₂	0·0155	0·95	0·0894	6·43
B ₂ O ₃	0·0317	1·95	0·0148	1·07
As ₂ O ₃	0·0018	0·11	0·0021	0·15
Cl	0·5740	35·39	0·4391	31·57
Br	trace	—	0·0034	0·25
H ₂ S	nil	—	0·0002	0·01
O(basic)	0·0185	1·14	0·0419	3·02
Fe	trace	—	trace	—
Al	0·0048	0·29	0·0009	0·06
Ca	0·0146	0·90	0·0015	0·11
Mg	0·0018	0·11	0·0006	0·04
K	0·0745	4·60	0·0267	1·92
Na	0·3190	19·67	0·3666	26·36
Li	0·0030	0·19	0·0056	0·40
Am	0·0012	0·08	0·0000	—
HCl	0·0008	0·05	—	—
Totals	1·6220	100·00	1·3908	100·00

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	As ₂ O ₅ .	H ₂ O.	Total.
I. trace	—	—	34·94	48·79	16·27	100·00
II. 49·83	4·74	18·00	17·37	10·62	100·56	

An analysis of the water from the Constant Geyser is given (III). Its temperature was 198° F.; reaction slightly acid; sp. gr. 1·0011. For the purpose of comparison, an analysis (IV) is given of the water from the Old Faithful Geyser in the Upper Geyser Basin. Its reaction is alkaline, and sp. gr. 1·00096.

In analysis IV traces of manganese, cæsium,* and rubidium were observed.

B. H. B.

Organic Chemistry.

Action of Chlorine on Amylene. By J. KONDAKOFF (*Chem. Centr.*, 1887, 979, from *J. Russ. Chem. Soc.*, 1887, 337).—In the course of investigations on the action of chlorine on isomeric amylenes, the author obtained from the modification insoluble in sulphuric acid, an unsaturated chloro-derivative, C_5H_9Cl , in addition to the dichloropentane $C_5H_{10}Cl_2$. From the former, two alcohols are obtainable, one a primary, boiling at 141° , and on oxidation yielding a caproic acid, the other a secondary alcohol, boiling at 117° , and yielding a ketone of boiling point $101-103^\circ$, probably methyl propyl ketone. The primary alcohol is a β -ethyl allyl alcohol, $CH_2Me \cdot CH \cdot CH \cdot CH_2 \cdot OH$; the secondary alcohol differs both from methyl isopropenyl carbinol and ethyl vinylcarbinol, and probably has the constitution $CHMe \cdot CH \cdot CHMe \cdot OH$.

V. H. V.

Action of Hypochlorous Acid on the Hydrocarbon C_8H_{18} . By S. A. PŘIBYTEK (*Chem. Centr.*, 1887, 978, from *J. Russ. Chem. Soc.*, 1887, 338).—The hydrocarbon $CH_2 \cdot CMe \cdot CH_2 \cdot CH_2 \cdot CMe \cdot CH_2$, obtained by Sesukoff from sodium and chlorisobutylene when treated with hypochlorous acid, yields a chlorhydrin, $C_8H_{14}(OH)_2Cl_2$, from which the dioxide $C_8H_{14}O_2$ can be obtained. The latter gives with water a tetratomic alcohol, *octylerythrol*, $C_8H_{14}(OH)_4$.

V. H. V.

Ammonio-zinc Cyanides. By R. VARET (*Compt. rend.*, 105, 1070—1072).—Pure zinc cyanide is dissolved to saturation in aqueous ammonia at a gentle heat and a current of ammonia gas is passed into the liquid, which is filtered when saturated with the cyanide, again treated with ammonia gas, and allowed to cool. A crystalline precipitate forms, but redissolves when gently heated, and separates on cooling in large, transparent, prismatic crystals of the composition $ZnCy_2 \cdot 2NH_3 + H_2O$. This compound loses ammonia and water when exposed to the air, and becomes white and opaque. It is very soluble in aqueous or alcoholic ammonia, and if freshly prepared, is also soluble in water with slight decomposition, but if it has been prepared for some time, it is immediately decomposed by water. It is slowly decomposed by sodium hydroxide in the cold. When heated

* "Calcium" in the original."

in a current of ammonia gas, it loses water, but no compound richer in ammonia is formed.

When zinc cyanide is dissolved to saturation in alcohol, treated with a current of ammonia gas, and the liquid allowed to evaporate spontaneously, the compound $\text{ZnCy}_2 \cdot 2\text{NH}_3$ is obtained in transparent crystals, which lose ammonia rapidly when exposed to the air and become opaque, and are very soluble in aqueous or alcoholic ammonia. The same compound is obtained by passing ammonia gas over gently heated zinc cyanide. Zinc cyanide forms only one compound with ammonia, and not a series of compounds like the chloride and bromide.

C. H. B.

Methyl Mercaptan and some of its Derivatives. By J. OBERMEYER (*Ber.*, **20**, 2918—2928).—Methyl thioacetate is prepared by the action of lead methyl mercaptide on a slight excess of cooled acetic chloride; it boils at $95-96^\circ$ (not $62-68^\circ$, Cahours, *Compt. rend.*, **80**, 1317, and **81**, 1163). The substance described by Cahours (*loc. cit.*) is probably a mixture of the ether with methyl iodide, acetic acid, and hydrobromic acid.

Methyl thiopropionate, $\text{C}_4\text{H}_8\text{SO}$, prepared from propionic chloride, is a colourless liquid of repulsive odour, boiling at $119-120^\circ$.

Methyl thiobutyrate, $\text{C}_5\text{H}_{10}\text{SO}$, is a light oil having an odour resembling that of butyric acid; it boils at $140-144^\circ$.

Methyl α -thiobenzoate, $\text{C}_8\text{H}_8\text{SO}$, boils at $231-232^\circ$.

Methylisopropyl sulphide, SMePr , is prepared by dissolving sodium in isopropyl mercaptan diluted with absolute ether, and the mixture, contained in a reflux apparatus, is treated with methyl iodide in small portions; it is then heated for 15 minutes in a water-bath and filtered. The heavy oil which separates from the solution when kept over night, is removed, and the ethereal solution evaporated and fractionally distilled. It boils at $93-95^\circ$.

Methyl amyl sulphide, $\text{SMe} \cdot \text{C}_5\text{H}_{11}$, is prepared by the action of methyl iodide on amyl mercaptide; it boils at $136-138^\circ$. Isoamyl disulphide is also formed.

Methyl allyl sulphide, $\text{SMe} \cdot \text{C}_3\text{H}_5$, is formed when 25 grams of lead methyl mercaptide is heated with allyl bromide and ether at 100° . It is a clear liquid of a very penetrating odour, boiling at $91-93^\circ$.

When allyl tribromide is heated with an excess of lead methyl mercaptide and ether at 100° , a compound, probably of the formula $\text{SMe} \cdot \text{C}_3\text{H}_4\text{Br}$, is obtained. It could not be purified, as it decomposes at $120-130^\circ$.

Methyl benzyl sulphide, $\text{SMe} \cdot \text{C}_7\text{H}_7$, is obtained by heating lead methyl mercaptide, and benzyl chloride at 100° . It is a clear liquid of an odour resembling horse-radish, and boils at $195-198^\circ$.

Methyl phenyl sulphide, $\text{SMe} \cdot \text{Ph}$, prepared from lead thiophenol and methyl iodide, forms a clear liquid boiling at $187-188^\circ$.

Dimethyl thioresorcinol, $\text{C}_6\text{H}_4(\text{SMe})_2$, is an oily liquid of a disagreeable odour boiling at 278° .

Methyl diphenyl sulphide, $\text{SMe} \cdot \text{C}_{12}\text{H}_9$, is obtained from lead thiodiphenyl; it crystallises from alcohol in flakes of very slender needles, melting at $107-108^\circ$.

Dimethyl diphenyl disulphide, $C_{14}H_{14}S_2$, is prepared by heating the lead mercaptide of diphenylthiohydrate with methyl iodide. It crystallises from alcohol in lustrous bright-yellow plates melting at $185-186^\circ$.
N. H. M.

Brandy from a Wine from Charente Inférieure. By E. C. MORIN (*Compt. rend.*, 105, 1019—1022).—The composition of the brandy in 100 litres is as follows:—Aldehyde, traces; ethyl alcohol, 50837 grams; normal propyl alcohol, 27·17; isobutyl alcohol, 6·52; amyl alcohol, 190·21; furfuraldehyde and bases, 2·19; fragrant oil, 7·61; acetic and butyric acids, traces; isobutylenic glycol, 2·19; glycerol, 4·38. There is no normal butyl alcohol, and amyl alcohol constitutes five-sixths of the higher alcohols. The fragrant oil is one of the constituents to which the wine owes its bouquet. (Compare Abstr., 1887, 714 and 746.)
C. H. B.

Production of Normal Amyl Alcohol by the Fermentation of Glycerol by *Bacillus Butylicus*. By E. C. MORIN (*Compt. rend.*, 105, 816—818).—When glycerol undergoes fermentation by *Bacillus butylicus* under the conditions determined by Fitz, 4 per cent. of the alcohols formed is normal amyl alcohol, boiling at $137-138^\circ$; refractive index at $13\cdot5^\circ$ for D = $1\cdot414$.

It is worthy of note that all the alcohols produced by *B. butylicus* are normal.
C. H. B.

Action of Zinc Methyl on Valeraldehyde. By J. KUVSINOFF (*Chem. Centr.*, 1887, 987—988, from *J. Russ. Chem. Soc.*, 1887, 204). *Methyl isobutyl carbinol* is produced when zinc methyl is added to well-cooled valeraldehyde, and the product of the action decomposed with ice-water. It is a light, mobile liquid, boiling at 130° , sp. gr. $0\cdot8271$ at 0° ; its *acetate* boils at 147° , sp. gr. = $0\cdot8805$ at 0° ; its *ketone* boils at $116-116\cdot5^\circ$, and on oxidation yields isopropylacetic, isobutyric, acetic, and formic acids, and is therefore identical with methyl isobutyl ketone.
V. H. V.

Action of Zinc Isoamyl and Zinc Isobutyl on Aldehyde. By E. SOKOLOFF (*Chem. Centr.*, 1887, 988, from *J. Russ. Chem. Soc.*, 1887, 197—204).—When zinc isoamyl is added to aldehyde, kept cool, and the resultant product decomposed with ice-water and distilled, methyl isoamyl carbinol is obtained besides isopropylethylene, and ethyl and isoamyl alcohols. The first yields an *acetate* boiling at $166-168^\circ$, and a *ketone* boiling at $143-145^\circ$, which yields on oxidation isopropylacetic acid. Zinc isobutyl when treated in like manner yields isobutyl and ethyl alcohols.
V. H. V.

Methyl Isopropenyl Carbinol. By J. KONDAKOFF (*Chem. Centr.*, 1887, 981, from *J. Russ. Chem. Soc.*, 1887, 336).—When treated with a 6 per cent. hydrochloric acid solution, methyl isopropenyl carbinol is converted into the isomeric trimethylethylene glycol. The readiness with which this change is effected is dependent on the

atomic arrangement; this has also been observed in the case of unsaturated acids.

V. H. V.

Iodide of Starch. By H. B. STOCKS (*Chem. News*, **56**, 212—213).—The author takes exception to the four points set forth by F. Mylius (*Abstr.*, 1887, 568), and makes the following remarks on each point. (1.) He states that iodide of starch is produced by the action of solutions of pure iodine, or of the vapour of iodine, on moist starch. (2.) That a limited amount of chlorine produces the blue colour in mixtures of hydriodic acid, or of an iodide, with starch; but that excess of chlorine destroys the colour, probably by the formation of a colourless chlorine compound of starch and iodine chloride. (3.) Silver nitrate does decolorise the iodide by removing the iodine as silver iodide, the colour being reproduced on the addition of either iodine or hydriodic acid; the action in the latter case may, however, be assumed to be due to iodine set free by the nitric acid liberated from the silver nitrate. (4.) Aqueous solutions of iodine do produce the blue colour with starch.

Water is necessary for the production of iodide of starch; therefore solutions of iodine in absolute alcohol do not colour dry starch blue. The blue iodide is destroyed by heat, the iodine being, in open vessels, partially volatilised, partially converted into hydriodic acid; in closed vessels, on the other hand, it is entirely converted into hydriodic acid. This decomposition is quick or slow according as the quantity of iodine is smaller or greater. By adding iodine to a solution decolorised in this manner, the blue colour is again formed, and this decolorisation and recolorisation may be frequently repeated with the same starch. Exposure to sunlight also decolorises iodide of starch. Iodide of starch is not affected by alcohol, ether, benzene, or carbon bisulphide; in fact, iodine may be removed from its solutions in the last two solvents by means of starch-paste.

Iodide of starch dissolves to a certain extent in water, and is precipitated from the solution by absolute alcohol, by dilute hydrochloric, sulphuric, and nitric acids, by strong hydrochloric acid, and by salts which do not react with it, such as sodium chloride. Strong nitric and strong sulphuric acid decompose it. Starch solutions are not precipitated by dilute acids like the solution of the iodide.

D. A. L.

Constituents of Rice-starch. By L. SOSTEGNI (*Chem. Centr.*, 1887, 896, from *Stud. di Chim. Agr. di Pisa*, **6**, 48—68).—The results quoted of the amount of dextrose obtained by the saccharification of starch accord with those of Salamon. In the course of the preparation of starch cellulose by Schulze's method, a fat melting at 47—48° was extracted; the crude fatty acids obtained therefrom melt at 50—51°; the proportion of fat found was 15 to 20 per cent. of the cellulose. The portion of residue, insoluble in ether, obtained in the saccharification of starch, differs from cellulose by its solubility in a 2 per cent. solution of potash, and its partial decomposition when warmed. From its solution, acetic acid precipitates an amorphous substance, turning brown in the air, soluble in Schweizer's reagent when moist, but not when dry; it is decomposed when boiled with

hydrochloric acid. The author regards starch cellulose as a mixture of cellulose with the derivatives of the latter substance or a modification of granulose. V. H. V.

Lichenin. By M. HÖNIG and S. SCHUBERT (*Monatsh.*, **8**, 452—465).—As there was considerable doubt whether the carbohydrate from Iceland moss (*Cetraria islandica*) was a single substance or a mixture of two or more, the authors have reinvestigated it. The dried and sorted moss was treated repeatedly with a 1 to 2 per cent. solution of K_2CO_3 . A pale-green mass quite free from the original bitter taste was thus obtained. This was then boiled for some time with water and filtered through linen. The filtrate on cooling deposited a gelatinous precipitate, which separated better when the solution was frozen. The liquid still contained some of this gelatinous substance, together with an easily soluble starch. The gelatinous precipitate, for which the authors propose to utilise the name *lichenin*, previously used for the whole extract, is very sparingly soluble in cold water, but dissolves in boiling water to an opalescent solution, which is at once cleared by the addition of a little potash. The greater part is precipitated from its solutions on cooling, or on the addition of alcohol. It is not coloured by iodine. When heated with dilute sulphuric acid, it very readily yields a crystalline dextrose, which gives a rotation $[\alpha]_D^{20} = +55.52^\circ$, and closely resembles, if it is not identical with, ordinary dextrose. The intermediate dextrin-compounds are tasteless and non-rotatory. The above-mentioned soluble carbohydrate, for which the authors propose the name *lichen-starch*, could not be obtained free from lichenin. It is strongly rotating, the rotation increasing the freer the starch is from lichenin. It is easily soluble in water, but is thrown down as a flocculent precipitate by alcohol. The highest rotation obtained was $[\alpha]_D^{20} = +102.82^\circ$. It is coloured blue by iodine. Diastase converts it readily into a dextrin showing rotation $[\alpha]_D^{20} = 162.44^\circ$. Lichenin is not affected by diastase. Lichen-starch, therefore, appears to be a soluble, unorganised modification of ordinary starch. L. T. T.

Reactions of Chloral. By O. REBUFFAT (*Gazzetta*, **17**, 406—409).—Chloral and sodium acetate, in presence of acetic anhydride, do not react in accordance with Perkin's reaction; the change is for the most part more profound, leading to the destruction of the molecule of chloral. Sodium acetate at a low temperature combines directly in equimolecular proportions with sodium acetate to form a compound, $C_2Cl_3HO, C_2H_3O_2Na$, which is white and minutely crystalline; it is decomposed by water and by alcohol to form chloral alcoholate. Experiments were also made with the anhydrides of other fatty acids, but without success. V. H. V.

Trithioacetaldehydes. By W. MARCKWALD (*Ber.*, **20**, 2817—2818; compare *Abstr.*, 1886, 864).— γ -Trithioacetaldehyde, when mixed with four times its weight of ethyl iodide and allowed to remain in a closed vessel for some weeks, suddenly undergoes conversion into a crystalline mass of the β -derivative. This change is not due to

the presence of free iodine in the ethyl iodide, since the change does not take place when an ethereal solution of the γ -aldehyde containing a small quantity of iodine is similarly treated. W. P. W.

Metallic Derivatives of Acetylacetone. By A. COMBES (*Compt. rend.*, **105**, 868—871).—The author has previously shown that acetylacetone has the constitution $\text{CH}_2\text{Ac}\cdot\text{COMe}$, and that the hydrogen of the CH_2 -group is readily displaced by chlorine or by sodium.

Acetylacetone and its homologues act on metallic salts like true acids, and yield a new series of crystalline compounds of the general formula $\text{M}(\text{C}_5\text{H}_7\text{O}_2)_n$, in which M is a metal with a valency n . The sodium and potassium derivatives form white, hexagonal prisms belonging to the rhombic system, and are most readily obtained by adding the required quantity of sodium or potassium ethoxide to an alcoholic solution of acetylacetone. They are somewhat soluble in absolute alcohol, but are insoluble in ether.

The magnesium salt is obtained by mixing acetylacetone with an excess of magnesium carbonate. There is rapid effervescence, and the filtered liquid when evaporated in a vacuum, deposits transparent, colourless, hexagonal prisms belonging to the rhombic system, which are anhydrous when dried at 125° . The aluminium compound is formed in the preparation of acetylacetone, and is also obtained by the action of the latter compound on a slightly acid solution of aluminium chloride. It is insoluble in water, somewhat soluble in alcohol, but less soluble in ether. When the solution is concentrated, it deposits nacreous crystals of the same form as the preceding compound, but they are readily decomposed by heat.

The copper salt is obtained in pale blue needles of the same form, when a somewhat concentrated solution of cupric acetate is mixed with a warm saturated aqueous solution of acetylacetone. The compound is insoluble in water, and in moderately dilute solutions the precipitation of the copper is complete. Larger crystals are formed when a dilute solution of cupric chloride is added to a boiling solution of acetylacetone. The crystals are anhydrous when dried at 125° .

Ferric chloride and acetylacetone yield a dark-red solution, the formation of which may be used as a test for the ketone, and when this is extracted with ether the red compound is dissolved. When the ether evaporates, the iron salt is deposited in bright-red crystals, similar in form to those of the ammonium salt.

The lead salt is formed by the action of lead carbonate on the ketone, is soluble in water, and resembles the magnesium compound in its crystalline form.

Acetylacetone behaves in fact like a monobasic acid. The sodium and potassium salts are, however, decomposed by hot water, with formation of acetone and an alkaline acetate, and the aluminum and iron compounds are not decomposed by ammonia in alcoholic solution. The sodium salt and methyl iodide yield a new derivative, *methyl-acetylacetone*, boiling at 165° , which has acid properties similar to those of the original compound. It seems, in fact, that the group $\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot$ has the properties which characterise the group COOH ,

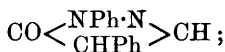
except that the two hydrogen-atoms cannot act successively. Salts of the type $C_6H_5O_2M$, in which M is a bivalent metal, have not yet been obtained, but the homologues of acetylacetone form salts of the type $(C_6H_5RO_2)_nM$, in which R is an alkyl radicle, and M is a metal of valency n .
C. H. B.

Preparation of α -Bromo-acids. By J. VOLHARD (*Annalen*, 241, 141—163).—Very good yields of α -brominated acids may be obtained by a slight modification of Hell's process (Abstr., 1881, 711). The action of the bromine and phosphorus on the acid, or preferably the crude anhydride, is carried on in a flask provided with a reflux condenser, instead of in sealed tubes. The bromine and the other ingredients must be free from moisture. The bromide is slowly dropped into boiling water, in order to convert it into the monobrominated acid. The following compounds were prepared: α -monobromosuccinic acid forms four-sided prisms, and melts at 159° . The ethyl salt boils at 150 — 160° under 50 mm. pressure, and the methyl salt at 132 — 136° under 30 mm. pressure. α -Monobromosuccinic acid is decomposed by boiling with water, yielding fumaric acid. α -Bromopropionic acid forms prismatic crystals melting at 24.5° , and α -bromisovaleric acid melts at 40° , and distils at 230° with slight decomposition.

W. C. W.

Ethereal Salts of Aldehydo-acids. By W. WISLIZENUS (*Ber.*, 20, 2930—2934).—When a mixture of ethyl acetate and ethyl formate is added by drops to twice the amount of ether in which sodium is placed, and the product decomposed by dilute sulphuric acid, an oil is obtained which gives an intense blue-violet colour with ferric chloride, and reacts with phenylhydrazine. The compound is probably *ethyl formylacetate*, $COH \cdot CH_2 \cdot COOEt$. It could not be purified; when kept in a desiccator, crystals of ethyl trimesate melting at 133° , separate. The yield of the latter is better than that obtained by Piutti's method (Abstr., 1887, 491).

Ethyl phenylformylacetate, $COH \cdot CHPh \cdot COOEt$, is prepared by suspending dry sodium ethoxide in absolute ether (3 parts), adding a mixture of ethyl phenylacetate and ethyl formate, and keeping the whole for several days in a closed vessel. The product is shaken with water, being kept cold with ice, and the aqueous solution is treated with sulphuric acid and extracted with ether. The ethereal extract is washed with soda, filtered, and freed from ether in a vacuum. The residue, consisting of a crystalline substance and an oil, is filtered, and the oil distilled in a vacuum. It boils at 144 — 145° under 16 mm. pressure. When boiled with dilute aqueous soda, it is decomposed into phenylacetic and formic acids; the free acid could not be obtained. The alcoholic solution of the ethereal salt gives a very intense blue-violet coloration with ferric chloride. It reacts readily with phenylhydrazine, with formation of the compound



this crystallises in plates melting at 195 — 196° , and is soluble in alkali, sparingly soluble in ether.

The crystalline compound obtained in the preparation of ethyl phenylformylacetate is readily purified by crystallisation from ether; it has the same composition as ethyl phenylformylacetate; it gives no colour reaction with ferric chloride. The liquid isomeride changes slowly at the ordinary temperature into the crystalline compound, but the change is immediate at the melting point of the crystals, 69—71°. The crystalline compound is also decomposed by alkali into formic and phenylacetic acids.

Ethyl methylformylacetate, $\text{COH}\cdot\text{CHMe}\cdot\text{COOEt}$, is a colourless oil, of agreeable odour, and boils at 160—162°; it gives an intense red-violet coloration with ferric chloride, and yields a pyrazoline-derivative with phenylhydrazine.

The above ethereal salts are derivatives of the half-aldehyde of malonic acid which v. Pechmann assumed (*Ber.*, 17, 936) to exist as an intermediate product in the synthesis of cumalinic acid.

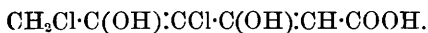
N. H. M.

Conversion of Benzene-derivatives into Fatty Compounds by the Action of Chlorine in Alkaline Solution. By A. HANTZSCH (*Ber.*, 20, 2780—2795).—When phenol (at most 50 grams) is dissolved in a moderate excess of aqueous soda (sp. gr. = 1.12), and the solution, after dilution with 2 to 3 times its volume of water, is treated at 0° with chlorine, the colour changes through green to brown, and a liquid or semi-solid brown mass separates; this dissolves on the addition of more alkali, but subsequently the solution slowly deposits a grey or black powder insoluble in alkali, and finally by alternating the addition of chlorine and alkali a point is reached, indicated by the dull-yellow colour of the solution, beyond which chlorination must not be carried. After precipitation of trichlorophenol by hydrochloric acid, a compound, *trichlorodihydroxyamanyl-carboxylic acid*, $\text{C}_6\text{H}_3\text{Cl}_3\text{O}_4$, is extracted by ether from this solution, and is obtained by cautious evaporation of the ether as an oil, which is best purified by heating it with aqueous ammonia, recrystallising the ammonium salt, decomposing this with sulphuric acid, extracting with ether, and repeatedly recrystallising from water. The acid crystallises in slender, white needles, which are anhydrous, and melt at 176—177° with complete decomposition; once, however, large, efflorescent, seemingly monoclinic crystals containing 4 mols. H_2O were obtained. It has a sour and yet distinctly sweet taste, is unaltered by exposure to the air, dissolves readily in water, alcohol, and ether, and when boiled in aqueous solution decomposes with evolution of hydrogen chloride. Under the conditions given, the yield of the acid was 50 per cent. The acid is monobasic, and the *ammonium salt*, $\text{C}_6\text{H}_4\text{Cl}_3\text{O}_4\cdot\text{NH}_4 + 2\text{H}_2\text{O}$, is the most characteristic compound; this crystallises in lustrous, rhombic prisms, has a neutral reaction and very sweet taste, is sparingly soluble in water with partial decomposition, and is not rendered anhydrous by exposure over sulphuric acid or by heating; it decomposes at 123°. The remaining salts are readily soluble with the exception of the *mercurous salt*, which crystallises in stellate groups of needles, and is converted into a dense, white, microcrystalline powder by heating with water. Concentrated alcoholic potash completely decomposes the acid with

the formation of chloride and carbonate. The *methyl* salt, $C_6H_4Cl_3O_4Me$ crystallises in needles, melts at 126° , and is insoluble in water. The acid does not form derivatives with hydroxylamine and phenylhydrazine, but yields with acetic anhydride a *diacetyl*-derivative, $C_6H_3Cl_3O_4Ac_2$, which crystallises best from acetic acid, melts at $188-192^\circ$ with complete decomposition, and is insoluble in cold water.

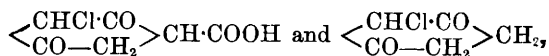
When the acid, or better its ammonium salt, is treated with zinc-dust and ammonia, or preferably with sodium-amalgam, and the product after acidification is extracted with ether, *dichlorodihydroxy-amenylcarboxylic acid*, $C_6H_3Cl_2(OH)_2\cdot COOH$, is obtained. This very closely resembles the trichloro-acid, and melts at $176-177^\circ$; it differs from it, however, by readily crystallising in large, lustrous prisms, by yielding an ammonium salt which does not crystallise well and melts at 185° , and by forming an *acetyl*-derivative melting at $132-134^\circ$. Concentrated aqueous soda converts the acid into a *sodium* salt, $C_6H_3ClO_4Na_2 + 6H_2O$, crystallising in canary-yellow needles. The corresponding acid could not be isolated, but salts were prepared, and these, with the exception of the copper salt which is green, are yellow. The sodium salt gives with ferric chloride a brownish-yellow precipitate, which dissolves in excess of the reagent to a dark-green solution. The salt is unstable and decomposes on heating with water, the solution becoming alkaline, whilst mineral acids, even in the cold, destroy its colour, and convert it, with the evolution of carbonic anhydride, into a white, microcrystalline acid of the composition $C_6H_5ClO_2$. This substance is very unstable; it melts at $96-97^\circ$ with complete decomposition into a carbonaceous mass, and is sparingly soluble in water; soluble in alcohol and ether, yielding solutions from which, with the exception of the last, the compound cannot again be obtained by crystallisation. The salts are intensely coloured; the *sodium* salt, $C_6H_5ClO_2Na + 3H_2O$, which can also be obtained from dichlorodihydroxyamenylcarboxylic acid by heating with concentrated aqueous soda at 100° , is readily soluble in water, very sparingly soluble in excess of aqueous soda, and crystallises in scales.

With regard to the constitution of these derivatives, the formula $CH_2Cl\cdot C(OH)\cdot CCl\cdot C(OH)\cdot CCl\cdot COOH$ is ascribed to the compound $C_6H_5Cl_3O_4$, termed trichlorodihydroxyamenylcarboxylic acid. In support of this view, it is urged that, together with the acid, the symmetrical trichlorophenol $[OH : Cl : Cl : Cl = 1 : 2 : 4 : 6]$ is always obtained, and that the acid can be readily prepared from this trichlorophenol under conditions similar to those employed in the case of phenol, 10 grams of trichlorophenol yielding 7 grams of the ammonium salt of the acid. It is probable, therefore, that the further action of chlorine in alkaline solution causes the benzene-ring in trichlorophenol to break at the point 1 : 2 or 1 : 6. To dichlorodihydroxyamenylcarboxylic acid is assigned the constitution



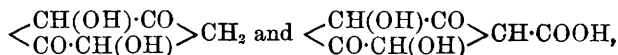
The compound $C_6H_5ClO_4$ derived from it is the carboxylic acid of the compound $C_6H_5ClO_2$, which despite its acid character is not a true acid, since it does not yield an ethyl salt either by treatment in alcoholic solution with hydrogen chloride, or by the action of ethyl

iodide on its sodium salt. With bromine, it does not form additive but only substitution derivatives; ammoniacal silver nitrate and cuprous chloride are not precipitated by it, and its sodium salt, when treated with phenylhydrazine acetate, yields an amorphous *phenylhydrazide*, whose composition approximates to that required by the formula $C_5H_5Cl(N_2PhH)_2$. The formulæ



are ascribed to the two compounds, which are termed *chlorodiketopentamethylenecarboxylic acid* and *chlorodiketopentamethylene* respectively, and the analogy between these and derivatives of the similarly constituted diketohexamethylene-derivatives is pointed out in the paper.

It has not been found possible as yet to displace the remaining chlorine-atom in chlorodiketopentamethylene, but it is possible to simultaneously withdraw all the chlorine from trichlorodihydroxy-amenylcarboxylic acid. When the acid, or preferably its ammonium salt, is treated with a considerable excess of concentrated baryta-water, and heated to about 60° , *barium dihydroxydiketopentamethylene-carboxylate*, $C_5H_2O_6Ba_2 + 4H_2O$, separates as a bright-yellow powder, insoluble in water. This salt effervesces on the addition of acetic acid, and is converted into the *barium* salt of *dihydroxydiketopentamethylene*, $C_5H_2O_4Ba + 3\frac{1}{2}H_2O$, which very closely resembles the preceding salt. Dihydroxydiketopentamethylene could not be prepared in the pure state; it is obtained as a yellow oil from the barium salt by treating it with hydrochloric acid and extracting with ether, and shows at first a tendency to crystallise, but very rapidly decomposes. It dissolves readily in water, reduces silver nitrate, and yields a compound with phenylhydrazine. The formulæ



are assigned to dihydroxydiketopentamethylene and its carboxylic acid respectively.

Trichlorophloroglucinol on treatment with baryta yields neither the trichloro-acid nor any of its decomposition products, whilst phloroglucinol and the three dihydroxybenzenes, when treated in a similar manner to phenol, do not yield crystalline ammonium salts, but only acid syrups, which on reduction with zinc-dust and ammonia give monochloroacetic acid in large quantity, but no dichlorodihydroxy-amenylcarboxylic acid.

Bromine, under precisely similar conditions to the above, does not act on phenol further than to produce tribromophenol.

W. P. W.

Derivatives of Isosuccinic Acid. By G. KÖRNER and A. MENOZZI (*Gazzetta*, 17, 425—441).—In continuation of a former paper on α -amido-isosuccinic acid, or α -isoaspartic acid (Abstr., 1887, 801), the salts are more fully described. The sodium salt, $C_4H_5NO_4Na$, crystallises either in needles with 1 mol. H_2O from concentrated solutions, or in prisms with 4 mols. H_2O in large, transparent prisms. The potas-

sium salt is anhydrous. The calcium, magnesium, zinc, cadmium, lead, copper, and silver salts are described, as also the compounds it forms with hydrochloric and nitric acids. The *methyl* salt, formed from methyl iodide and the silver salt, crystallises in white needles; when the potassium salt is heated with methyl iodide, the *betaine potassio-iodide*, $C_4H_3NMe_3O_4K_2I \cdot 7H_2O$, is produced; it is very hygroscopic, and forms an *aurochloride*, $C_4H_3NMe_3ClO_4 \cdot AuCl_3$, a yellow, insoluble precipitate.

Amido- α -isosuccinamic acid, or *α -isoasparagine*,



obtained by heating the neutral amide with aqueous ammonia in sealed tubes, forms crystals with hexagonal base, more soluble in cold than in hot water; it forms a *copper* salt, $(C_4H_7N_2O_3)_2Cu$, crystallising in small tables.

Amido- α -isosuccinamide, $NH_2 \cdot CMe(CONH_2)_2$, obtained by heating pyruvic and hydrocyanic acids, and treating the resultant product with alcoholic ammonia, crystallises in tables with a rhombic base, sparingly soluble in cold, readily in hot water. When boiled with barium or potassium hydroxides it gives for each molecule two molecules of ammonia; it is decomposed only to a slight extent by magnesia. Its *hydrochloride*, *sulphate*, and *nitrate* crystallise in prisms, and are very soluble in water. V. H. V.

Oxidation of Copaiba Balsam. By S. LEVY and P. ENGLÄNDER (*Annalen*, **242**, 189—214).—The most important facts contained in this paper have already appeared in this Journal (Abstr., 1886, 250). The unsymmetrical dimethylsuccinic acid obtained by the oxidation of copaiba balsam is identical with the acid described by Barnstein (this vol., p. 135). The acid forms triclinic crystals [$a : b : c = 2.0294 : 1 : 1.1909$; $\alpha = 118^\circ 36'$, $\beta = 95^\circ 16'$, $\gamma = 101^\circ$]. The barium salt, $C_6H_8O_4Ba + 2\frac{1}{2}H_2O$, is monoclinic [$a : b : c = 1.6006 : 1 : 1.709$; $\beta = 97^\circ 26'$]. The salts of calcium, $C_6H_8O_4Ca + H_2O$, and ammonium, $C_6H_8O_4(NH_4)_2$ and $C_6H_8O_4 \cdot NH_4$, are crystalline. The normal sodium salt, $C_6H_8O_4Na_2 + 11H_2O$, forms silky prisms, and the acid salt, $C_6H_8O_4Na + 3\frac{1}{2}H_2O$, monoclinic prisms,

$$a : b : c = 1.83653 : 1 : 4.18006; \beta = 90^\circ 43'.$$

The anhydride of dimethylsuccinic acid melts at 29° . It unites with phenylhydrazine, forming dimethylsuccinylphenylhydrazine, a compound crystallising in monoclinic plates [$a : b : c = 1.05521 : 1 : 0.82996$; $\beta = 99^\circ 57'$]. It melts at 131 — 132° . The imide of dimethylsuccinic acid melts at 106° . W. C. W.

Dibromosebacic Acid and some of its Derivatives. By A. CLAUS and T. STEINKAULER (*Ber.*, **20**, 2882—2889).—*Dibromosebacic acid*, $C_{10}H_{16}Br_2O_4$, is prepared by heating sebacic acid and bromine ($2\frac{1}{2}$ mols.) at 160 — 170° for about three hours. The oily product solidifies after some hours to a crystalline mass which is freed from adherent oil by suction on porous plates. It crystallises from water in long, feathery needles melting at 115° (uncorr.), and is readily soluble in

alcohol, ether, chloroform, and benzene, sparingly soluble in boiling water. Prolonged boiling with water decomposes the acid and its salts with elimination of hydrobromic acid. Sulphuric acid dissolves it unchanged. The *sodium salt*, $C_{10}H_{14}Br_2O_4Na_2$, is a heavy white, crystalline substance, very readily soluble in water, from which it crystallises with 3 mols. H_2O . The *hydrogen potassium salt* is almost insoluble in cold water; the *barium* (with 2 mols. H_2O), *calcium* (with 2 mols. H_2O), *lead*, *silver*, *copper*, and *ammonium salts* were also prepared. The *methyl salt* crystallises in small, lustrous, rhombohedral plates melting at 50° (uncorr.); the *ethyl salt* is a thin oil.

Hydroxysebacic acid, $C_{10}H_{16}O_6$, is prepared by boiling sodium dibromosebate with water, evaporating to dryness on a water-bath, digesting over sulphuric acid, and extracting with absolute alcohol. The filtrate is neutralised with alcoholic soda. The sodium salt so obtained is converted into the insoluble lead salt which is then decomposed with hydrogen sulphide. The acid is readily soluble in hot water and in cold alcohol, from which it separates in small crystalline grains melting at 143° (uncorr.); it is very sparingly soluble in ether, insoluble in benzene and chloroform. The *sodium salt*, $C_{10}H_{14}O_6Na_2$, forms a white, sandy powder very readily soluble in water.

Dihydroxysebacic acid, $C_{10}H_{18}O_6$, is obtained by boiling an aqueous solution of dibromosebacic acid with freshly precipitated silver oxide; the product is filtered, treated with hydrogen sulphide, and evaporated to a syrup; this becomes crystalline when kept over sulphuric acid. It is very readily soluble in water, alcohol, and glacial acetic acid, sparingly soluble in ether, insoluble in benzene and chloroform; it melts at 130° (uncorr.) and is decomposed at a higher temperature. It is optically inactive. The *sodium salt*, $C_{10}H_{16}O_6Na_2$, is very soluble in water.

N. H. M.

Constitution of Levulinic and Maleic Acids. By A. MICHAEL (*Amer. Chem. J.*, 9, 364—372).—The reactions brought forward by Anschütz (Abstr., 1887, 916) in favour of the new constitutional formulæ suggested by Roser for maleic and levulinic acids are examined. It is shown that by assuming certain reactions for ketones or for aldehydes similar in kind to those already known, the syntheses and transformations of these two acids and also of several others such as their acetyl-derivatives, mucobromic acid, the dibromosuccinic acids, &c., are quite as easily explained by the old formulæ as by the new ones of Roser.

H. B.

Butenyltricarboxylic and Ethylsuccinic Acids. By G. POLKO (*Annalen*, 242, 113—126).—*Ethyl butenyltricarboxylate*,



is prepared by adding 48 grams of ethyl malonate to a warm solution of 6.9 grams of sodium in 77 grams of alcohol; 48.5 grams of ethyl α -bromobutyrate is added to the product. It is a pale-yellow liquid boiling between 271° and 281° . Its sp. gr. is 1.065 compared with water at 17° . The free acid is soluble in water, alcohol, ether, and acetone. It melts at 119° , and begins to decompose at 124° . The

barium salt, $\text{Ba}_3(\text{C}_7\text{H}_7\text{O}_6)_2$, and silver salt, $\text{Ag}_3\text{C}_7\text{H}_7\text{O}_6 + 1\frac{1}{2}\text{H}_2\text{O}$, are amorphous. The normal calcium salt, $\text{Ca}_3(\text{C}_7\text{H}_7\text{O}_6)_2$, is very hygroscopic. The acid salts, $\text{CaH}_4(\text{C}_7\text{H}_7\text{O}_6)_2$ and $\text{CaH}(\text{C}_7\text{H}_7\text{O}_6) + 2\frac{1}{2}\text{H}_2\text{O}$, are crystalline and insoluble in alcohol. The zinc, strontium, and potassium salts are amorphous.

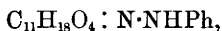
Ethylsuccinic acid, $\text{COOH}\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{COOH}$, is prepared by distilling butenyltricarboxylic acid. It is also formed in the saponification of ethyl butenyltricarboxylate. It melts at 97° and is identical with the α -ethylsuccinic acid described by Huggenberg (Abstr., 1878, 782). In addition to the salts described by Huggenberg, the crystalline strontium salt and the methyl salt were prepared. The latter boils at $202\text{--}205^\circ$. The anhydride remains liquid at -19° . Its sp. gr. at 34° is 1.165. The amide melts at 214° with decomposition. It is insoluble in cold water and in alcohol. W. C. W.

Isobutenyltricarboxylic Acid and Unsymmetrical Dimethylsuccinic Acid. By F. BARNSTEIN (*Annalen*, 242, 126—140).—*Ethyl isobutenyltricarboxylate*, $\text{COOEt}\cdot\text{CMe}_2\cdot\text{CH}(\text{COOEt})_2$, is prepared by the action of ethyl α -bromisobutyrate on ethyl sodiomalonate in alcoholic solution. It boils at $272\text{--}275^\circ$, and its sp. gr. is 1.064 compared with water at 17° . The free acid is difficult to obtain in the crystalline state. It is soluble in water, alcohol, ether, and acetone. On boiling the aqueous solution, carbonic anhydride is evolved. The acid melts at 120° with decomposition, yielding unsymmetrical dimethylsuccinic acid. The sodium, magnesium, barium and silver salts of isobutenyltricarboxylic acid are amorphous. The potassium salt, $\text{K}_3\text{C}_7\text{H}_7\text{O}_6 + 2\text{H}_2\text{O}$, forms efflorescent prisms. The calcium salts, $\text{Ca}_3(\text{C}_7\text{H}_7\text{O}_6)_2 + 9\text{H}_2\text{O}$ and $\text{Ca}(\text{C}_7\text{H}_7\text{O}_6)_2 + 2\text{H}_2\text{O}$, are crystalline.

Unsymmetrical dimethylsuccinic acid, $\text{COOH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{COOH}$, melts at 139° , and is freely soluble in alcohol, ether, acetone, and in hot water. It forms acid and normal salts. The normal salts of the heavy metals and alkaline earths are, as a rule, very sparingly soluble in water. The normal potassium salt is amorphous and deliquescent; the acid salt, $\text{C}_6\text{H}_8\text{O}_4\text{K} + 5\text{H}_2\text{O}$, crystallises in plates which effloresce on exposure to the air. The normal barium salt, $\text{C}_6\text{H}_8\text{O}_4\text{Ba} + 2\text{H}_2\text{O}$, is crystalline; the acid salt is also crystalline, and readily soluble in water. The cadmium salt, $\text{C}_6\text{H}_8\text{O}_4\text{Cd} + 6\text{H}_2\text{O}$, and the lead salt, $\text{C}_6\text{H}_8\text{O}_4\text{Pb} + \text{H}_2\text{O}$, are crystalline, and dissolve with difficulty in water. *Dimethylsuccinyl chloride*, $\text{C}_6\text{H}_8\text{O}_2\text{Cl}_2$, boils at $200\text{--}202^\circ$. *Diethyl dimethylsuccinate* boils at $213\text{--}215^\circ$. Its sp. gr. at 17° is 1.0134 compared with water at the same temperature. The *dimethyl salt* boils at 200° ; sp. gr. 1.0568 at 16° . *Dimethylsuccinic anhydride* boils at 215° . Thiophen-derivatives cannot be obtained by the action of phosphorus sulphide on unsymmetrical dimethylsuccinic acid. W. C. W.

Furfuran Derivatives. By W. MARCKWALD (*Ber.*, 20, 2811—2817; compare Abstr., 1876, ii, 444).—Furfuracrylic acid is best obtained by heating furfuraldehyde (1 part), sodium acetate (2 parts), and acetic anhydride (2 parts) at 250° for 11 hours; the yield amounts

to more than 80 per cent. of that theoretically possible. The ammonium salt of its reduction-product, furfuropropionic acid, is converted into *furfuropropionamide*, $C_6H_7O \cdot CONH_2$, by heating for several hours in a closed tube at 220° ; this crystallises in white needles, melts at 98° , distils at 270° without decomposition, is soluble in water, alcohol, ether, and benzene, sparingly soluble in light petroleum, and on treatment with bromine and aqueous potash does not yield the corresponding amine, since the furfuran nucleus alone is attacked. When furfuroacrylic acid (1 part) is heated with 95 per cent. alcohol (3.5 parts) and saturated with hydrogen chloride, the ethyl salt of a bibasic acid, $C_5H_8O(COOEt)_2$, is obtained as an oil which distils at 286° ; this is heavier than and insoluble in water, soluble in alcohol and ether in all proportions, and has a pleasant, aromatic odour and a very bitter taste; the yield amounts to more than 80 per cent. of that theoretically possible. When saponified, it yields the corresponding *acid*, $C_7H_{10}O_5$, which crystallises from water in large, colourless, transparent, thin prisms, melts at 138° , or with partial decomposition at about 110° when heated for some time in an open vessel, and has a very bitter taste. On distillation, it is converted into oily decomposition-products of partly acid and partly neutral character. The *barium*, *calcium*, *zinc*, and *copper* salts were prepared; the silver salt, $C_7H_8O_5Ag_2$, forms microscopic needles. Since the ethyl salt yields a *phenylhydrazide*,



the author ascribes to the acid the formula



and adduces the following evidence in its support; the acid is not reduced by sodium amalgam, does not form an additive compound with bromine, and on oxidation with dilute nitric acid is converted into succinic acid (the yield amounting to more than 40 per cent. of the acid employed), and a liquid fatty acid (? acetic or propionic acid). The acid is not acted on when heated at 200° with hydriodic acid saturated at 0° , whilst addition of amorphous phosphorus leads to experimental difficulties which have not yet been surmounted.

W. P. W.

Action of Nitric Acid on Symmetrical Trichlorobenzene. By C. L. JACKSON and J. F. WING (*Amer. Chem. J.*, **9**, 348—355).—In proving the constitution of benzenetrisulphonic acid (this vol., p. 152), it was found that with fuming nitric acid, symmetrical trichlorobenzene did not yield a mononitro-derivative melting at 68° (Beilstein and Kurbatow, *Annalen*, **192**, 233), but the dinitro-derivative melting at 130° . If sulphuric acid was used at the same time, the trinitro-derivative was obtained. Whether a mono-, di-, or tri-nitro-compound is obtained depends not only on the temperature and presence or absence of sulphuric acid, but also to a very considerable extent on the purity of the acid employed, an acid of sp. gr. 1.51, free from nitrogen peroxide, being more effective than one of sp. gr. 1.534 containing much nitrogen peroxide.

Trichlorobenzene (1 : 3 : 5) is best formed by the chlorination of di-

chloraniline prepared by Witt's method (this Journal, 1876, i, 264). *Trichlorodinitrobenzene*, $C_6HCl_3(NO_2)_2$, is produced at the ordinary temperature by the action of nitric acid of sp. gr. 1.505 on trichlorobenzene. It crystallises from alcohol in white prisms melting at 129.5° . The mononitro-compound is readily obtained by boiling with nitric acid of sp. gr. 1.46. *Trichlorotrinitrobenzene*, $C_6Cl_3(NO_2)_3$, is prepared by using a mixture of fuming sulphuric acid and nitric acid of sp. gr. 1.505. It crystallises from alcohol in nearly white needles melting at 187° .
H. B.

Action of Sulphuric Acid on Bromodurene. By O. JACOBSEN (*Ber.*, 20, 2837—2840).—When bromodurene is treated with eight times its weight of sulphuric acid at the ordinary temperature, and the mixture allowed to remain for 10 to 12 days, a thick brown liquid is obtained, which, on the addition of ice and subsequently of water, yields a residue consisting chiefly of dibromodurene, together with hexamethylbenzene and unaltered bromodurene. The aqueous solution was free from halogenated sulphonic acids, but contained at least three sulphonic acids, one of which on hydrolysis yields prehnitene, whilst the other two yield pseudocumene. From these results, the author concludes that sulphuric acid acts in this case as a bromine-carrier, converting the bromodurene into dibromodurene and durene (compare Neumann, *Abstr.*, 1887, 573), the latter of which in the presence of sulphuric acid yields pseudocumene, prehnitene, and hexamethylbenzene in the manner already described by him (*Abstr.*, 1887, 660).

Dibromodurene, under similar conditions, is not acted on by sulphuric acid.

Probably sulphuric acid acts as a bromine-carrier when in its presence bromobenzene and paradibromobenzene are converted into dibromobenzenesulphonic acid and a mixture of tetra- and hexabromobenzene respectively, as observed by Herzig (*Abstr.*, 1882, 46). The author has also found that dibromometaxylene, [Me : Me : Br : Br = 1 : 3 : 4 : 6], when treated with chlorosulphonic acid, yields the chloride of its sulphonic acid together with a considerable quantity of tetrabromometaxylene, although but a small quantity of the latter results when the same dibromometaxylene is heated with sulphuric acid at 240° , an isomeric liquid dibromometaxylene being the chief product in this case.
W. P. W.

Aniline Salts. By A. DITTE (*Compt. rend.*, 105, 813—816).—*Aniline molybdate*, $2NH_2Ph.3MoO_3.5H_2O$, forms hard, brilliant, transparent, prismatic crystals, which lose water when gently heated, and decompose at a higher temperature. It is obtained by mixing a warm concentrated solution of ammonium molybdate with excess of a concentrated solution of aniline hydrochloride. Oily drops separate and rapidly change to a crystalline precipitate, and when this is dissolved in hot water and the solution cooled, the salt crystallises in radiating groups.

Aniline tungstate, $2NH_2Ph.4WO_3.3H_2O$, analogous to ammonium metatungstate, forms long, brilliant, transparent needles, which lose

water when gently heated, and at a higher temperature burn with a smoky flame leaving a residue of tungstic anhydride. When ammonium tungstate is mixed with a boiling solution of aniline hydrochloride, no reaction takes place, but if aniline is added, a portion of it dissolves, and when the still acid liquid is concentrated and cooled, the aniline tungstate crystallises.

Three aniline vanadates can be obtained. Warm solutions of ammonium vanadate and aniline hydrochloride yield a red liquid, acid to litmus; when this is cooled, it deposits yellow needles of the composition $\text{NH}_2\text{Ph}, \text{V}_2\text{O}_5, 4\text{H}_2\text{O}$, which darken on exposure to light, and at 100° lose water and become green with a metallic lustre. At a higher temperature, the salt blackens and decomposes. If a small quantity of aniline is added to the mixed solutions in the experiment just described, and the black precipitate which forms filtered off, a reddish-brown liquid is obtained, which after some hours deposits brilliant, reddish-brown needles of the composition $4\text{PhNH}_2, 3\text{V}_2\text{O}_5, 18\text{H}_2\text{O}$. They lose water when heated, and decompose at a higher temperature. If aniline is added gradually in small quantities with constant agitation to a cold concentrated solution of equal equivalents of aniline hydrochloride and ammonium vanadate, small yellow crystals separate. The solution is diluted until these crystals dissolve, and aniline is added until it no longer dissolves. The liquid is then concentrated over sulphuric acid, when the compound $2\text{NH}_2\text{Ph}, \text{V}_2\text{O}_5, 2\text{H}_2\text{O}$ crystallises in large pale-yellow plates mixed with reddish-brown crystals of the preceding compound.

Aniline iodate, $\text{NH}_2\text{Ph}, 2\text{I}_2\text{O}_5$, is obtained by mixing a cold almost saturated solution of ammonium iodate with an excess of aniline hydrochloride. It forms brilliant, white, nacreous plates, which alter when exposed to light, but may be kept in the dark at a low temperature. When gradually heated, it at first seems to undergo no alteration, but below a red heat it detonates very violently. If ammonium diiodate is used instead of the normal salt, decomposition of the salt begins at the moment of its formation.

Aniline chlorate is obtained in needles by mixing cold concentrated solutions of sodium chlorate and aniline hydrochloride. It is very unstable, and decomposes rapidly even in the dark at 0° . At the ordinary temperature, it quickly becomes black, and detonates violently at about 20° .

Aniline borate, $\text{NH}_2\text{Ph}, 2\text{B}_2\text{O}_3, 4\text{H}_2\text{O}$, analogous to ammonium baborate, is obtained by mixing the ammonium salt with aniline hydrochloride, or more easily by adding aniline to a boiling saturated solution of boric acid, in which it is readily soluble. The filtered liquid when cooled first deposits unaltered aniline, and then unctuous, transparent, white lamellæ, which lose water when heated, then intumesce and give off alkaline vapours, and finally take fire at a higher temperature.

C. H. B.

Homologues of Aniline and their Separation on a Large Scale. By O. N. WITT (*Chem. Ind.*, 10, 8—13).—In the present communication, the author, after detailing the progress made in the manufacture of pure benzene, toluene, and xylene, since 1880, refers

to the processes of separating the homologues of aniline on a commercial scale. The two nitrotoluenes are best isolated by freezing out part of the para-compound, and separating part of the ortho-derivatives by fractional distillation with steam. The medium portion is then reduced, and the toluidines thus obtained are subjected to a separation process, based on the fact that on treating a mixture of ortho- and para-toluidine with sulphuric acid insufficient in quantity to saturate both isomerides, the para-compound is first attacked. Hence on subjecting such mixtures to distillation, aided by the introduction of steam, a distillate rich in orthotoluidine is obtained. The latter may then be further purified by repeating the above treatment. The residual paratoluidine sulphate is neutralised with caustic soda or lime, and the base separated by distillation and recrystallisation. The separation of para- and meta-xylydine may be effected by sulphonating both isomerides; metaxylydinesulphonic acid is insoluble, whilst the acid from the para-compound is freely soluble, but yields an almost insoluble sodium salt, from which the base may be obtained by distillation with addition of a small amount of lime. To isolate the base from the meta-acid, the latter is heated at 160—180° under pressure with five times its weight of hydrochloric acid. The acid mixture is then saturated with soda or lime, and subjected to distillation with steam. D. B.

Butylenic Bases: Characteristics of Ethylenic Diamines.

By A. COLSON (*Compt. rend.*, 105, 1014—1016).—10 grams of isobutylene bromide, boiling at 147—149°, was heated to boiling for 10 minutes with 40 c.c. of aniline, the excess of aniline expelled by distillation in a vacuum, and the aniline hydrochloride removed by treatment with water. The residue was then dissolved in warm hydrobromic acid, and the crystals which separated on cooling were purified by washing with hydrobromic acid. *Diphenylbutylenediamine hydrobromide*, $C_6H_5(C_2H_4N)_2 \cdot 2HBr$, is thus obtained in white crystals, which melt at 122° with decomposition. It dissolves in five times its weight of boiling water, and 10 times its weight of cold water with partial decomposition, which is prevented if hydrobromic acid is present. It is about twice as soluble in alcohol as in water, but is not soluble in ether. The hydrobromide is decomposed completely by alkaline hydroxides with liberation of the base as a colourless oil, insoluble in water, but soluble in alcohol, ether, and chloroform. It has a bitter burning taste, and is coloured brown by nitric acid; its sp. gr. is about 1.0. With hydrochloric acid it yields a hydrochloride crystallising in white nodules, which become blue when exposed to air, melt at 98°, and dissolve in 10 times their weight of cold water with some decomposition. With acetic acid, the base forms a viscous acetate which is soluble in water, and seems to be uncrystallisable.

The aqueous solution of the base has no action on any indicator, and the alcoholic solution has no action on phthaleins, but decolorises methyl-orange. In this respect, it resembles ethylenediphenyldiamine and ethyleneditolyldiamine, and hence it would seem that secondary aromatic diamines containing ethylene are distinguished from primary amines such as aniline and toluidine, by the fact that

they are very feebly basic, and do not act on phthaleins, but decolorise methyl-orange. The basic properties decrease as the molecular weight increases.

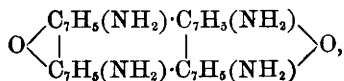
When diphenylbutylenediamine hydrobromide is treated with sodium nitrite at 0° it yields a nitroso-derivative in the form of a yellow precipitate which melts at 90° . C. H. B.

Azopseudocumene. By V. POSPĚCHOFF (*Chem. Centr.*, 1887, 858—859, from *J. Russ. Chem. Soc.*, 1887, 113—118).—Nitropseudocumene when reduced with sodium amalgam, yields *azopseudocumene*, $N_2(C_6H_3Me)_2$, which forms yellowish crystals melting at 173 — 174° , and may be sublimed without decomposition. It is sparingly soluble in alcohol, more readily in ether and benzene; it dissolves in concentrated sulphuric acid, but is reprecipitated on dilution.

The corresponding hydrazo-derivative is obtained by reducing nitropseudocumene with zinc-foil; it melts at 124 — 125° , and is readily oxidised in the air to the azo-derivative. In both cases, cumidine is obtained as a bye-product. V. H. V.

Formation of Aniline Dyes by the Oxidation of Aromatic Amines. By J. BARZLOFFSKY (*Chem. Centr.*, 1887, 855—857, from *J. Russ. Chem. Soc.*, 1887, 132—149).—By the oxidation of aromatic amines, azo-compounds and polyamines are formed; by changing certain conditions, basic products are formed which play an important part in the aniline dye industry. In order to throw some light on the nature of the chemical changes involved, the products of the oxidation of paratoluidine were investigated. The principal compounds formed are parazotoluene and *azotolyl*, $C_{28}H_{26}N_4$, the latter of which may also be obtained from hydroparazotoluene by heating its alcoholic solution with concentrated hydrochloric acid, as also by the oxidation of toluidine. The formation of azotolyl by the oxidation of paratoluidine is explained thus: two atoms of hydrogen are removed from two molecules of toluidine with production of hydrazotoluene, of which one part is converted into azotoluene by further oxidation, whilst the other part is transformed into the isomeric tolidine, which passes by oxidation into azotolyl.

Azotolyl when heated with an alcoholic solution of ammonium sulphite is readily transformed into the corresponding hydro-derivative, which differs from its analogues in readily combining with acids, and being separable on addition of alkalis. The hydrochloride, $(C_7H_7, HCl) + 1\frac{1}{2}HO$, is colourless in the pure state, but when damp is readily oxidised to a compound, *pararosotoluidine*,



which is also obtained by oxidation of a dilute solution of paratoluidine with large excess of chromic acid, and subsequent addition of soda to the resultant product. V. H. V.

Formation of Dyes by means of Hydrogen Peroxide. By C. WURSTER (*Ber.*, **20**, 2934—2940).—Ammonia is added to an emulsion of phenol and water so that a part of the phenol remains undissolved; a solution of sodium carbonate and an equal volume of hydrogen peroxide are added, and the whole diluted with water. The mixture is well shaken, a crystal of a hydroxylamine salt added, and the whole again shaken; a bright-blue and then a deep-blue coloration is produced which in a day or two changes to green. The dye which is extracted with ether is shown to be phenolquinonimide.

Hydrogen peroxide is found in the sap of many plants; it is also produced by micro-organisms, especially by the non-pathogenic.

All the monatomic phenols of the benzene series examined, in which the para-position to the hydroxyl-group is free, gave quinone-imides with hydrogen peroxide and ammonia. Hydroxy-acids also yield dyes.

Lacmoid is formed when an ammoniacal solution of resorcinol is boiled with a little hydrogen peroxide.

If sodium carbonate is added to a mixture of resorcinol and quinone, a deep-green solution is obtained which, when shaken with air becomes yellow, then reddish-yellow and brownish-red; when air is removed, the green colour is regenerated. A similar change of colour is observed in many leaves, especially those of *Berberis* which contain a considerable amount of hydrogen peroxide.

Pyrocatechol, orcinol, and some plant constituents, such as phloridzin, also give dyes with hydrogen peroxide. N. H. M.

Formation of Safranines. By P. BARBIER and L. VIGNON (*Compt. rend.*, **105**, 939—941).—It has been shown that phenosafranine is formed by oxidising a mixture of paraphenylene diamine (1 mol.) and aniline (2 mols.), and it is known that amidoazobenzene yields paraphenylenediamine on reduction. It therefore seemed probable that the action of nitrobenzene or amidoazobenzene in presence of some reducing agent evolving hydrogen, should yield phenosafranine, and this supposition is confirmed by experiment.

Amidoazobenzene hydrochloride (1 mol.) is mixed with iron and hydrochloric acid in sufficient quantity to yield one molecular proportion (H_2) of hydrogen, and sufficient nitrobenzene to form a paste, and heated at 188° for three hours. The product is diluted with water, and treated with a current of steam to remove unchanged aniline; the aqueous solution is then mixed with ammonia, filtered, and the safranine precipitated by adding sodium chloride. The phenosafranine which separates is purified by repeated precipitation by means of salt and recrystallisation from hot water.

Amidoazotoluene likewise yields a safranine when heated with nitrobenzene, and hence it seems that this constitutes a general reaction for the preparation of safranines. C. H. B.

Nitro-derivatives of Oxanilide. By W. G. MIXTER and F. O. WALTHER (*Amer. Chem. J.*, **9**, 355—361).—Huebner and Rudolph's work on paradinitro-oxanilide is confirmed. *Tetranitrooxanilide*, $C_6O_2[NH \cdot C_6H_3(NO_2)_2]_2$ [$NH : (NO_2)_2 = 1 : 2 : 4$], is formed by the

action of red fuming nitric acid on oxanilide; it melts at 300° , is but slightly soluble, and is easily saponified by weak potash. *Hexanitro-oxanilide*, $C_2O_2[NH \cdot C_6H_2(NO_2)_3]_2[NH : (NO_2)_3 = 1 : 2 : 4 : 6]$, is obtained when a mixture of fuming nitric acid and strong sulphuric acid is employed; it is the highest substitution product obtainable. It melts at 300° , its best solvent is glacial acetic acid. When heated with sulphuric acid at 200° , it yields a trinitraniline melting at 188° , which is the melting point of the only known trinitraniline, $NH_2 : (NO_2)_3 = 1 : 2 : 4 : 6$. In alkaline solutions, it dissolves with formation of trinitrophenyloxanilide, trinitrophenol, and trinitraniline.

Trinitrophenyloxamide, $NH_2 \cdot CO \cdot CO \cdot NH \cdot C_6H_2(NO_2)_3$, crystallises in white fibres, and melts with decomposition at $255-260^{\circ}$. It has strongly marked acid characters. The potassium and ammonium salts are described.

H. B.

Nitro-derivatives of Dibromoxanilide. By W. G. MIXTER and C. P. WILLCOX (*Amer. Chem. J.*, **9**, 361—364).—*Dinitrodibromoxanilide*, $C_2O_2(NH \cdot C_6H_3Br \cdot NO_2)_2[NH : NO_2 : Br = 1 : 2 : 4]$, is obtained by the action of strong nitric acid on paradibromoxanilide. It is yellow, melts at 288° , and when saponified yields orthonitroparabromaniline, melting at 111.4° .

Tetranitrodibromoxanilide, $C_2O_2[NH \cdot C_6H_2(NO_2)_2Br]_2$, is obtained with some difficulty by using red fuming nitric acid. It is white, melts at $285-287^{\circ}$, and does not yield dinitrobromaniline when saponified.

H. B.

Compounds of Alloxan with Aromatic Amines. By G. PELLIZZARI (*Gazzetta*, **17**, 409—425).—Alloxan combines directly with the aromatic amines to form additive products from which, however, the base cannot be recovered as such. Thus when a concentrated boiling aqueous solution of alloxan is agitated with α -naphthylamine, and the solution cooled, a compound of the formula $C_{14}H_{11}N_3O_4$ separates $C_4H_2N_2O_4 + C_{10}H_7NH_2 = C_{14}H_{11}N_3O_4$. This compound, *α -naphthylamine-alloxan*, crystallises in transparent, colourless needles, insoluble in water, acids, aqueous ammonia, but soluble in ether, benzene, and chloroform; it is coloured greenish by concentrated sulphuric acid. When heated with alkalis, it dissolves, yielding ammonia and the potassium salt of an acid, $C_{14}H_{10}N_2O_5$; on acidification, the acid separates in long, glistening needles, insoluble in ether, benzene, and chloroform, but very soluble in alcohol. At 110° , it loses the elements of a molecule of water, but takes it up again on recrystallisation from aqueous alcohol. β -Naphthylamine apparently does not combine with alloxan.

Aniline combines with alloxan to form *phenylamine-alloxan*,



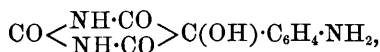
which crystallises in scales, decomposing at 248° . It forms a *hydrochloride*, $C_{10}H_9N_3O_4 \cdot HCl$, which crystallises in transparent needles, and a *silver salt*, $C_{10}H_8AgN_3O_4$, a white, insoluble powder. Like the naphthyl-derivative, it yields an acid, $C_9H_8N_3O_5$, when boiled with

alkalis, thus: $C_{10}H_8N_3O_4 + H_2O = C_9H_8N_2O_3 + NH_3 + CO_2$. This acid crystallises in colourless needles which decompose at 180° without fusion; it is soluble in alkalis and their carbonates; its *silver* salt, $C_9H_7AgN_2O_3$, is a white crystalline precipitate. On dry distillation, phenylamine-alloxan yields *paratoluidine*.

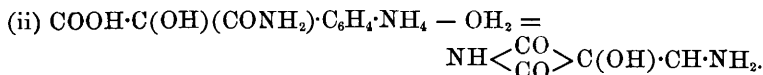
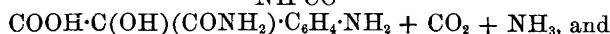
Methylphenylamine-alloxan, $C_{11}H_{11}N_3O_4 = C_4H_2N_2O_4 + NHPhMe$, crystallises in white scales soluble in alcohol, moderately soluble in boiling water; its *hydrochloride*, $C_{11}H_{11}N_3O_4 \cdot HCl$, forms colourless prisms.

Dimethylphenylamine-alloxan, $C_{12}H_{13}N_3O_4 + H_2O$, crystallises in colourless needles, sparingly soluble in water, and decomposing at 230° . Its *hydrochloride* crystallises in transparent needles, the *nitrate* in lozenge-shaped crystals, the *oxalate* in quadrangular tables; the silver salt is a white precipitate. This compound, like the preceding, is decomposed by alkalis with formation of an acid.

To these derivatives, of which that of aniline is selected as a typical example, the author ascribes either the formula



or $COOH \cdot NH \cdot CO \cdot C(CONH_2) : C_6H_3 \cdot NH_2$, of which the latter illustrates at once the basic and acid character, as also its decomposition by alkalis to form an acid, $C_9H_8N_2O_3$, by elimination of ammonia and carbonic anhydride, thus: $COOH \cdot NH \cdot CO \cdot C(CONH_2) : C_6H_3 \cdot NH_2 + H_2O = COOH \cdot C(CONH_2) : C_6H_3 \cdot NH_2 + NH_3 + CO_2$. On the other hand, the combination of the benzene nucleus with another grouping by two of its carbon-atoms is unusual. The other formula illustrates the formation of paratoluidine by the dry distillation of the aniline compound, whilst the production of the acid compound is explained as a result of two successive reactions, in the first of which a carboxylic acid is formed which subsequently gives off a molecule of water to produce an imide, thus: $CO < \begin{smallmatrix} NH \cdot CO \\ NH \cdot CO \end{smallmatrix} > C(OH) \cdot C_6H_4 \cdot NH_2 + 2H_2O =$



If the latter formula be correct, then the above compounds might be considered as derivatives of dialuric acid or tartronyl carbamide.

V. H. V.

Benzylidenephthalide and Isobenzalophthalide. By S. GABRIEL (*Ber.*, 20, 2863—2868).—Benzylidenephthalide crystallises in small, monoclinic forms; $a : b : c = 1.9005 : 1 : 2.3830$; $\beta = 76^\circ 2.5'$.

Benzylphthalimidine (Abstr., 1885, 902, 1229) is readily obtained by adding a mixture of benzalophthalimidine (12 grams) and amorphous phosphorus (6 grams) to 36 c.c. of boiling hydriodic acid (b. p. = 127°), and subsequently heating for 45 minutes in a reflux apparatus. The yield amounts to 80 per cent. of that theoretically possible. When treated with phosphorus oxychloride,

and heated on a water-bath until hydrogen chloride ceases to be evolved, a product is obtained which, after extraction with water, solution in alcohol, and precipitation with ammonia, crystallises from benzene in orange- or cinnabar-red, slender needles of the composition $C_{15}H_{11}N$. This compound is soluble in chloroform, but only very sparingly in alcohol, has feeble basic properties, and forms unstable purple salts which are soluble in alcohol, and could not be analysed with the exception of the *picrate*, $C_{36}H_{25}N_5O_7$, a salt crystallising in cantharides-green prisms appearing reddish-violet by transmitted light. Phthalimidine also yields with phosphorus oxychloride a black powder having a bronze lustre; this is insoluble in all ordinary reagents and dissolves in sulphuric acid with a dark blue colour.

When isobenzalphthalide is heated with methylamine and alcohol for nine hours at 100° , it is converted into β -desoxybenzoincarboxyl-methylamide, $COPh \cdot CH_2 \cdot C_6H_4 \cdot CO \cdot NMeH$; this crystallises from benzene in snow-white, matted needles, melts at 143 – 144° , and when heated at 200° is converted into its constituents.

Nitrobenzylidenephthalide, on reduction with hydriodic acid and amorphous phosphorus, yields in addition to isobenzalphthalide a white powder; this crystallises from acetic acid in colourless, compact needles, begins to sinter at 240° , melts at 255 – 257° , and dissolves in aqueous soda or potash yielding yellow crystals of the corresponding salt. The crystals have the composition $C_{15}H_{11}NO_2$. When the compound (1 gram) is heated with methyl alcohol (10 c.c.), potassium hydroxide (1.7 gram) and methyl iodide (3 grams) at 100° for one hour, two compounds are obtained of the composition $C_{15}H_{10}NO_2Me$; one of these crystallises out on cooling in colourless, compact crystals, which begin to sinter at 200° , melt at 235 – 237° , and are sparingly soluble in alcohol, insoluble in alkalis, whilst the second remains in the mother-liquor and crystallises from alcohol in long, colourless needles melting at 119 – 121° . Since the compound is not a lactone, its constitution is probably expressed by one of the two formulæ $C_6H_4 < \begin{smallmatrix} C(OH) : CPh \\ CO - NH \end{smallmatrix} >$ or $C_6H_4 < \begin{smallmatrix} CO \cdot CHPh \\ CO - NH \end{smallmatrix} >$.

W. P. W.

Benzyl-derivatives. By S. GABRIEL and H. HENDESS (*Ber.*, **20**, 2869–2872).—*Metanitrobenzylphthalimide*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot N : C_6H_4O_2$, is formed when an intimate mixture of metanitrobenzyl chloride (1.7 gram) and potassium phthalimide (2 grams) is heated at 120° for about one hour. It crystallises in slender needles, melts at 155° , and is soluble in acetic acid and alcohol, sparingly soluble in water. When heated with fuming hydrochloric acid at 200° for two hours, it is converted into a mixture of phthalic acid and *metanitrobenzylamine hydrochloride*; the latter crystallises in needles. Metanitrobenzylamine yields an *acetyl-derivative*, $C_7H_7N_2O_2Ac$, crystallising in needles which melt at 91° , and a *platinochloride*, $(C_7H_5N_2O_2)_2 \cdot H_2PtCl_6$, crystallising in rhombic scales, whilst reduction with tin and hydrochloric acid converts it into *metamidobenzylamine*; this dissolves in water, has a strongly alkaline reaction, and forms a

picrate crystallising in sparingly soluble scales and a *platinochloride*, $C_7H_8(NH_2)_2, H_2PtCl_6$, crystallising in yellow scales.

Benzaltetrachlorophthalide, $CHPh : C \begin{smallmatrix} \text{O} \\ \text{C}_6\text{Cl}_4 \end{smallmatrix} > CO$, is obtained when tetrachlorophthalic anhydride (10 parts) is heated with phenylacetic acid (5 parts) and sodium acetate ($\frac{1}{4}$ part). It crystallises in slender, yellow needles, melts above 360° , and is practically insoluble in acetic acid and hot alcohol, more soluble in hot benzene and nitrobenzene. On treatment with sodium hydroxide, it is converted into α -tetrachlorodesoxybenzoïnorthocarboxylic acid, $CH_2Ph \cdot CO \cdot C_6Cl_4 \cdot COOH$, which crystallises in colourless needles, melts at 175° , dissolves readily in alcohol, ether and benzene, and yields a *barium* salt, $(C_{15}H_7Cl_4O_3)_2Ba$, crystallising in pale rose-coloured needles.

Dichlorophthalic anhydride, when similarly treated, yields *benzaldichlorophthalide*, $CHPh : C \begin{smallmatrix} \text{O} \\ \text{C}_6H_2Cl_2 \end{smallmatrix} > CO$, which crystallises in small, brownish-yellow needles, melts at 210° , dissolves readily in benzene, and by the action of alkalis is converted into α -dichlorodesoxybenzoïnorthocarboxylic acid, $C_{15}H_{10}Cl_2O_3$, crystallising in colourless needles melting at 117° .

W. P. W.

Resazoïn and Resorufin. By E. EHRLICH (*Monatsh.*, 8, 425—428).—Brunner and Kraemer (Abstr., 1884, 1333) proposed to drop the prefix *di-* from the names diazoresorcinol and diazoresorufin, but the author and Benedikt, contending that these compounds are no more azo- than diazo-derivatives, suggest re-naming them *resazoïn* and *resorufin*.

Resazoïn when dissolved in potash and oxidised with hydrogen peroxide yields *hydroxyresazoïn*, $C_{18}H_{12}N_2O_7$. This substance crystallises in almost colourless needles or scales which decompose before fusion, yielding a slight crystalline sublimate and leaving a carbonaceous residue. It is sparingly soluble in alcohol, soluble in glacial acetic and hydrochloric acids. Alkalis dissolve it with a reddish-yellow coloration. When reduced with zinc and sulphuric acid or ammonia, it yields a derivative of the formula $C_{18}H_{16}N_2O_7$, crystallising in needles.

These oxidation-derivatives confirm the correctness of Weselsky and Benedikt's formula $C_{18}H_{12}N_2O_6$ for resazoïn, but are not in keeping with Brunner and Kraemer's formula $C_{12}H_9NO_4$ (*loc. cit.*).

L. T. T.

Three Isomeric Tritolylstibines. By A. MICHAELIS and U. GENZKEN (*Annalen*, 242, 164—188).—The preparation of the tritolylstibines has been previously described by the authors (Abstr., 1884, 1135). Paratritolylstibine forms hexagonal rhombohedra [$a : c = 1 : 1.5807$]. Its sp. gr. at 15.6° is 1.35448 (water at $4^\circ = 1$). It melts at 127 — 128° and dissolves freely in chloroform. It forms additive chlorine, bromine, and iodine compounds which have already been described (*loc. cit.*). On the addition of a cold alcoholic solution of mercuric chloride to paratritolylstibine dissolved in alcohol and ether, tritolylstibinemercuric chloride is precipitated, $(C_6H_4CH_3)_3Sb, HgCl_2$, but if hot

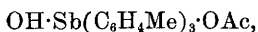
solutions are mixed, paratolylmercuric chloride, $C_6H_4Me \cdot HgCl$, is obtained.

Orthotritolylstibine, $Sb(C_6H_4Me)_3$, melts at $79-80^\circ$, and dissolves freely in chloroform, benzene, ether, and light petroleum. *Orthotolylmercuric chloride*, $C_6H_4Me \cdot HgCl$, is obtained as a crystalline powder on mixing ethereal solutions of mercuric chloride and mercury ditolyl. It melts at $145-146^\circ$. *Orthotritolylmercuric chloride* is freely soluble in chloroform and is deposited from alcohol in silky plates. Unlike the para-compound, the alcoholic solution is not decomposed on boiling, yielding tolylmercuric chloride.

In the preparation of orthotritolylstibine, needle-shaped crystals melting at 112° are obtained. The compound (probably orthoparatritolylstibine) is freely soluble in chloroform, benzene, ether, and light petroleum. With mercuric chloride, it yields a crystalline compound which melts at 164° with decomposition. The alcoholic solution is not decomposed on boiling.

Orthotritolylstibine chloride, $(C_6H_4 \cdot CH_3)_3SbCl_2$, melts at $178-179^\circ$, the *bromide* melts at $209-210^\circ$, and the *iodide* at $174-175^\circ$. The *oxide* melts at 220° and dissolves freely in acids.

Metatritolylstibine melts at $67-68^\circ$ and dissolves freely in ether, benzene, chloroform, and acetic acid. Its sp. gr. at 15.7° is 1.3957 compared with water at 4° . The additive compound with mercuric chloride melts with decomposition at 140° . The alcoholic solution is decomposed by boiling, yielding metatolylmercuric chloride, $C_6H_4Me \cdot HgCl$ (m. p. $159-160^\circ$). *Metatritolylstibine chloride* melts at $137-138^\circ$. It is very soluble in benzene, ether, and chloroform. The *bromide* has been previously described (*loc. cit.*). The *iodide* melts at $138-139^\circ$ and dissolves freely in chloroform, benzene, ether, and alcohol. The *oxide* is sparingly soluble in alkalis, alcohol, benzene, chloroform, and ether. The *basic acetate*,



is crystalline and melts at $142-143^\circ$. *Metatritolylstibine sulphide*, $SbS(C_6H_4Me)_3$, is obtained as a crystalline compound by the action of hydrogen sulphide on a solution of tritolylstibine chloride in alcoholic ammonia. It melts at $162-163^\circ$ and dissolves in chloroform and benzene. Chlorine, bromine, or iodine converts the sulphide (in solution in chloroform) into the corresponding chloride, bromide, or iodide.

W. C. W.

Decomposition of Isonitroso-compounds. By H. v. PECHMANN (*Ber.*, 20, 2904—2906; compare *Abstr.*, 1887, 1103).—*Benzoylformaldehyde hydrate*, $COPh \cdot CH(OH)_2$, is obtained as follows: nitrosoacetophenone is dissolved in a strong solution of hydrogen sodium sulphite, and the double compound so obtained boiled with 10 parts of 30 per cent. sulphuric acid; on cooling, the whole solidifies to a mass of white needles, which are dissolved out in ether and recrystallised from water. It forms lustrous, colourless needles, which melt at 73° and give off water at a higher temperature. The *anhydrous aldehyde* boils at above 142° under 125 mm. pressure. The hydrate has a peculiar penetrating odour, dissolves readily in the usual

solvents, reduces ammoniacal silver solution, and is converted into mandelic acid by alkalis. When the dilute aqueous solution is treated with some drops of ammonia, flakes separate which form spheres on adding acid.

Phenyltoluinoxaline (Hinsberg, *Annalen*, **237**, 370) is formed when an aqueous aldehyde solution is warmed with toluylenediamine sulphate and sodium acetate, and crystallises in colourless needles melting at 135°.

N. H. M.

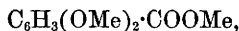
Negative Nature of Organic Radicles. By V. MEYER (*Ber.*, **20**, 2944—2952).—It was shown previously that desoxybenzoïn and benzyl cyanide, when treated with sodium ethoxide and an alkyl iodide, yield derivatives in which one hydrogen-atom of the methylene-group is replaced by an alkyl radicle, whilst ethyl phenylacetate does not react under similar conditions (*Abstr.*, 1887, 572). This reaction has now been extended to a large number of aromatic compounds containing carbonyl- and methylene-groups, and it is found that the hydrogen of the methylene-group is displaceable by an alkyl radicle only in compounds precisely analogous in constitution to desoxybenzoïn and benzyl cyanide. Under these conditions, the amides $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NEt}_2$ and $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NPh}_2$, the phenylpropionitrile, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CN}$, the nitrile of cinnamic acid, $\text{CHPh}:\text{CH}\cdot\text{CN}$, and methyl diphenylacetate, $\text{CHPh}_2\text{COOMe}$, do not yield alkyl-derivatives; aceto- and butyro-nitrile are unattacked; whilst dibenzyl ketone, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$, paraphenylenediace-tonitrile, $\text{CN}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CN}$, and derivatives of the type $\text{COR}\cdot\text{CH}_2\cdot\text{R}'$, containing complex aromatic radicles (naphthyl, phenanthryl, &c.) readily form alkyl-compounds. The sulphone, $\text{SO}_2\text{Ph}\cdot\text{CH}_2\text{Ph}$, a compound which crystallises well and volatilises without decomposition, does not react with sodium ethoxide and alkyl iodides. Di- and tri-phenylmethane also do not yield alkyl-derivatives when similarly treated, whilst beautiful, violet-coloured compounds are formed by the action of sodium ethoxide on the nitro-derivatives of these hydrocarbons.

Further investigation has shown that under no condition can more than one hydrogen-atom of the methylene-group present in desoxybenzoïn be displaced by an alkyl radicle. Nor is it possible to effect a substitution of an alkyl radicle for the remaining hydrogen-atom of the methylene-group in benzoïn, $\text{COPh}\cdot\text{CHPh}\cdot\text{OH}$, or its acetyl-derivative, $\text{COPh}\cdot\text{CHPh}\cdot\text{OAc}$. Diphenylacetone-nitrile, CHPh_2CN , a well-characterised crystalline compound, however, is readily acted on by sodium ethoxide and haloïd alkyl-derivatives. The substitution of methyl in the phenyl-group of benzyl cyanide does not seem to interfere with the production of alkyl-derivatives, since the three isomeric methylbenzyl cyanides, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CN}$, react with sodium ethoxide and benzyl chloride just as readily as benzyl cyanide itself, although the yield of the product $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}(\text{C}_6\text{H}_7)\cdot\text{CN}$ is not quite the same in each case.

Like nitroethane and ethyl acetoacetate, desoxybenzoïn and benzyl cyanide combine with nitrous acid, diazobenzene, &c. The diazo-derivatives have little stability and are difficult of isolation; the

isonitroso-compounds, $\text{CO}\cdot\text{Ph}\cdot\text{CPh}\cdot\text{N}\cdot\text{OH}$ and $\text{CN}\cdot\text{CPh}\cdot\text{N}\cdot\text{OH}$, can readily be obtained; the latter crystallises well and is distinctly acid in character. W. P. W.

Derivatives of Dimethyl- α -Resorcylic Acid. By H. MEYER (*Monatsh.*, 8, 429—438).—*Methyl dimethyl- α -resorcylicate*,



crystallises in prisms, melts at 81° , boils at 298° , and sublimes in white needles. *Methyl monomethyl- α -resorcylicate*, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{COOMe}$, which is also formed during the methylation of dimethyl- α -resorcylic acid, forms an oil boiling with partial decomposition at 315° . *Nitro-dimethyl- α -resorcylic acid*, $\text{NO}_2\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{COOH}$, may be formed either by heating the solid acid with nitric acid, or by adding nitric acid to an acetic acid solution of the acid. It crystallises in yellow needles or prisms, is sparingly soluble in water, easily in alcohol and glacial acetic acid, and melts at 225° , subliming at a higher temperature. It forms well-marked salts, of which those of the alkalis are easily, the others sparingly, soluble in water. On reduction, it yields *amidodimethyl- α -resorcylic acid*, $\text{NH}_2\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{COOH}$, which crystallises in hexagonal plates, easily soluble in alcohol, sparingly in water, and melting with decomposition at 182° . Its *hydrochloride* and *stannochloride* crystallise in needles. The *silver* and *copper* salts are very sparingly soluble in water. The amido-acid does not yield a quinoline-derivative, and consequently the amido- (respectively nitro-) group is probably in the para-position to the carboxyl-group.

When calcium dimethyl- α -resorcylicate is subjected to dry distillation, dimethylresorcinol distils over. The residue contains calcium carbonate, a resinous compound (probably an etheric-derivative of resorcinol), and the calcium salt of an acid which the author has not yet isolated. This acid melts at about 222° , gives a violet coloration with ferric chloride, and is therefore an ortho-hydroxy acid.

L. T. T.

Action of Phthalic Anhydride on Amido-acids. By L. REESE (*Annalen*, 242, 1—22).—Drechsel has shown (*Abstr.*, 1883, 1126) that phthalylamidoacetic acid is formed by the action of phthalic anhydride on glycocine, and he has described the properties of the acid and of several of its salts. The sodium salt is very soluble in water, but it is precipitated on the addition of alcohol to the solution. The precipitate has the composition $\text{C}_{10}\text{H}_6\text{NO}_4\text{Na} + \text{H}_2\text{O}$. The ammonium salt, $\text{C}_{10}\text{H}_6\text{NO}_4\text{NH}_4$, is prepared by adding alcoholic ammonia to an alcoholic solution of the acid; it melts at 205° with decomposition. The salt is very soluble in water; the aqueous solution loses ammonia on evaporation. When a cold solution of copper sulphate is added to the sodium salt, rhombic prisms or plates of a pale blue colour are deposited having the composition $(\text{C}_{10}\text{H}_6\text{NO}_4)_2\text{Cu} + 3\text{H}_2\text{O}$, but on mixing hot solutions the anhydrous salt is deposited in six-sided plates. When the copper salt is cautiously heated, phthalimide and benzoic acid sublime. The silver salt, $\text{C}_{10}\text{H}_6\text{NO}_4\text{Ag}$, is deposited from hot aqueous solutions in prisms. By the action of ethyl iodide on

this salt, the ethylic salt, $C_{10}H_9NO_4Et$, is obtained. It crystallises in needles, dissolves freely in ether, chloroform, and hot alcohol, melts at $104-105^\circ$, and distils at a temperature above 300° without decomposition. It is quickly saponified by boiling water.

Salts of glycocinephthalic acid are formed by neutralising hot aqueous solutions of the alkalis or alkaline earths with phthalylamidocaproic acid, and evaporating the solution. The sodium salt is amorphous. It is precipitated as a gelatinous mass on the addition of alcohol to the concentrated aqueous solution. The potassium salt is deliquescent, and crystallises in needles; the barium salt forms rhombic plates. The copper salt is deposited in needle-shaped crystals on the addition of the sodium salt to a solution of copper sulphate. The crystalline silver salt is soluble in hot water.

Phthalylamidocaproic acid, $C_{13}H_{15}NO_4$, is prepared by fusing a mixture of phthalic anhydride and leucine. The pure acid crystallises in needles, melts at $115-116^\circ$, and is soluble in alcohol and ether; on the addition of water to the alcoholic solution, the acid is deposited in the form of an oily liquid. The alcoholic solution is laevogyrate. On dry distillation, optically inactive phthalylamidocaproic acid is formed. The inactive acid can be recrystallised from hot alcohol and ether. It melts in boiling water, and the solution on cooling deposits a few crystals. The active acid forms a crystalline platodiammonium salt, $Pt(NH_3NH_3C_{13}H_{14}NO_4)_2 + 3H_2O$, insoluble in alcohol. The inactive acid forms a similar compound containing $3\frac{1}{2}$ mols. H_2O , which is less soluble in cold water than the salt of the optically active acid. The copper salt is amorphous. It is soluble in alcohol, and is decomposed by heat, yielding butylphthalimide.

The phthalylamidocaproic acids are converted by the action of alkalis into leucinphthalic acids, and finally into leucine and phthalic acid.

The sodium salt of the optically active leucinephthalic acid is amorphous, and is deposited as a gelatinous mass on the addition of alcohol to the aqueous solution. The potassium salt, $K_2C_{14}H_{15}NO_5$, is crystalline and freely soluble in water. The barium salt is crystalline and sparingly soluble. The platodiammonium salt forms rhombic plates freely soluble in water, sparingly soluble in alcohol, and insoluble in ether. The amorphous copper salt dissolves freely in alcohol. The free acid, $COOH \cdot C_6H_4 \cdot CO \cdot NH \cdot CH(COOH) \cdot CH_2Pr^a$, is soluble in alcohol and ether. It is decomposed by boiling water, yielding phthalic acid and leucine. It melts at $130-132^\circ$, and splits up into water and phthalylamidocaproic acid (active). The potassium salt of inactive leucinephthalic acid is deposited in crystals on the addition of alcohol to the aqueous solution. The silver salt is amorphous. The free acid melts at $152-153^\circ$, splitting up into inactive phthalylamidocaproic acid and water. It closely resembles the optically active acid in its properties.

W. C. W.

Action of Phthalyl Dichloride on Ethyl Sodiomalonate. By J. WISLIGENUS (*Annalen*, 242, 23-93).—By the action of phthalyl dichloride (1 mol.) on ethyl sodiomalonate (2 mols.) mixed with ether, a mixture of ethyl phthalylmalonate, dimalonate and phthaloxylidi-

malonate is obtained. The crude product is treated with water, and the ethereal solution evaporated. An oily liquid remains which deposits crystals of ethyl phthalylmalonate. In the course of a few days, ethyl phthaloxylmalonate is also deposited. On distilling the uncrystallisable mother-liquor in a current of steam, ethyl malonate volatilises; the non-volatile oil consists of ethyl phthalylmalonate. After it has been purified by washing with a solution of sodium carbonate, it solidifies, forming a crystalline mass.

Ethyl phthalylmalonate, $C_{15}H_{14}O_6$, is deposited from ether in triclinic prisms. The crystals are highly refractive. The ethereal salt dissolves in 14 times its weight of ether at 9° , and in 1.7 times its weight of ether at 35° . It is more soluble in alcohol. It melts at 74.5° , and on cooling the fused mass, the solidification proceeds from certain points in a peculiar and characteristic manner.

Ethyl phthaloxylmalonate, $C_{22}H_{24}O_8$, is deposited from ether in needles and from alcohol in prisms. It requires 184 parts by weight of ether at 9° , and 174 parts of absolute alcohol at 14° for solution. It is dissolved by alkalis with an intense yellow coloration. The substance melts at 116.5° if the temperature is slowly raised, and at 106° if it is quickly heated. In the latter case, it soon solidifies and melts again at 116.5° .

Ethyl phthalylmalonate, $C_{22}H_{26}O_{10}$, is deposited from hot alcohol in prisms melting at 48.5° . It is freely soluble in alcohol and ether.

Ethyl phthalylmalonate is decomposed by alkalis, yielding ethyl alcohol, and phthalic and malonic acids. It also splits up on boiling with water into ethyl malonate and phthalic acid. When reduced with zinc-dust and acetic acid, it unites with four atoms of hydrogen, forming *diethyl hydrogen benzylmaloncarboxylate*,



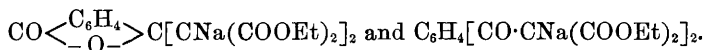
The formation of this monobasic acid is incompatible with the symmetrical formula for ethyl phthalylmalonate. The new compound is very soluble in alcohol and ether, but it requires 2230 times its weight of water at 17° for solution. It melts at 86° . The sodium salt is deliquescent and is precipitated by ether from its alcoholic solution. The silver salt, $C_{15}H_{17}AgO_6$, is soluble in hot water and is crystalline. On treatment with ethyl iodide, it yields triethyl benzylmaloncarboxylate, a colourless liquid boiling at 250° under 45 mm. pressure. *Dipotassium ethyl benzylmaloncarboxylate*, $C_8H_7(COOK)_2COOEt$, is formed when a solution of the potassium salt of diethylbenzylmaloncarboxylic acid is left in contact with potassium hydroxide for one hour at the ordinary temperature, but *benzylmalonorthocarboxylic acid*, $COOH \cdot C_6H_4 \cdot C_2H_3(COOH)_2$, is produced if the salt is boiled with an excess of alkali and then acidified. This acid is soluble in hot water. It begins to decompose at 170° , and at 180° it is completely converted into carbonic anhydride and the hydrocinnamorthocarboxylic acid described by Gabriel and Michael (Abstr., 1878, 426).

Phthalylidiamide, $C_8H_8N_2O_2$, is deposited in crystals when alcoholic ammonia is added to a solution of ethyl phthalylmalonate in absolute alcohol. It is insoluble in the usual solvents, and by boiling with water or by heating at 210° is decomposed, yielding phthalylimide.

Sodium ethoxide acts on ethyl phthalylmalonate, forming *ethyl phthaloyloxethylsodiummalonate*, $\text{CO} < \text{C}_6\text{H}_4 > \text{C}(\text{OEt}) \cdot \text{CNa}(\text{COOEt})_2$.

The sodium atom is easily displaced by hydrogen, yielding ethyl phthaloyloxyethylmalonate, a substance which is easily decomposed by warm alkalis, yielding ethyl alcohol, phthalic and malonic acids. *Ethyl phthaloyloxyethylmethylmalonate*, $\text{CO} < \text{C}_6\text{H}_4 > \text{C}(\text{OEt})\text{CEt}(\text{COOEt})_2$, is formed by the action of ethyl iodide on the preceding sodium compound. It is saponified by alcoholic potash at the ordinary temperature, but the product splits up into alcohol and the potassium salt, $\text{C}_{13}\text{H}_9\text{K}_3\text{O}_7$. On the addition of hydrochloric acid to a solution of the potassium salt, benzoylorthocarboxethylmalonic acid is liberated, but it spontaneously decomposes into phthalic and malonic acids. An oily liquid which behaves in a similar manner is obtained when an acid is added to the solution of ethyl phthalylmalonate in alkalis. It is probable that the sodium compound of ethyl phthalylhydroxymalonate is formed in the first instance, and that it is converted into ethyl phthalylhydroxymalonate, which at the ordinary temperature splits up into phthalic anhydride and ethyl malonate. At 100° , ethyl monochloracetate converts the ethyl phthaloyloxyethylsodiummalonate into the ethyl phthalylethylethenyltricarboxylate. On hydrolysis, this acid yields benzoylorthocarboxethenyltricarboxylic acid, which is decomposed by water, yielding ethenyltricarboxylic and phthalic acids.

Ethyl phthaloxydimalonate unites with potassium hydroxide, forming orange-coloured crystals of the composition $\text{C}_{22}\text{H}_{23}\text{KO}_{10}$. A yellow sodium compound, $\text{C}_{22}\text{H}_{24}\text{Na}_2\text{O}_{10}$, is produced by the action of an ethereal solution of ethyl phthalylmalonate on ethyl sodiummalonate. The sodium is displaced by ethyl on treatment with ethyl iodide, and the product is decomposed by alkalis into alcohol, ethylmalonic and phthalic acids. The yellow substance is probably a mixture of the two isomerides,



By the action of acetic anhydride, phthalic anhydride, or phthalic chloride on the yellow sodium compound, ethyl phthaloxylmalonate is formed, but glacial acetic acid decomposes the substance with the formation of ethyl malonate and ethylphthalylmalonate, together with small quantities of ethyl phthalylmalonate. Hot water also decomposes the sodium compound, yielding ethyl phthalylmalonate (from the unsymmetrical compound), and ethyl malonate and sodium phthalate from the symmetrical isomeride. It is decomposed by bromine into ethyl phthalylmalonate and ethyl dibromomalonate, $\text{C}_{22}\text{H}_{24}\text{Na}_2\text{O}_{10} + 2\text{Br}_2 = 2\text{NaBr} + \text{C}_{15}\text{H}_{14}\text{O}_6 + \text{CBr}_2(\text{COOEt})_2$. Ethyl phthaloxylmalonate unites with four atoms of nascent hydrogen, forming a neutral oil of the composition $\text{C}_{22}\text{H}_{28}\text{O}_9$. Ethyl phthaloxylmalonate is probably an unsymmetrical compound, having the constitution represented by the formula $\text{CO} < \text{C}_6\text{H}_4 > \text{C} : \text{C}(\text{COOEt})_2$.

Ethyl phthalylidimalonate dissolves in alkalis, forming an orange-coloured liquid. If the solution is heated at 100° for some hours, the colour disappears; on the addition of an acid, a tribasic acid, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{CH}_2\cdot\text{COOH})_2\cdot\text{OH}$, is liberated, which at once splits up into water and phthalylodiacetic acid, $\text{CO} < \underset{\text{O}}{\text{C}_6\text{H}_4} > \text{C}(\text{CH}_2\cdot\text{COOH})_2$.

A yellow potassium compound, $\text{C}_{22}\text{H}_{24}\text{K}_2\text{O}_{10} + 2\text{H}_2\text{O}$, is precipitated on the addition of ether to the orange-coloured solution of ethyl phthalylidimalonate in alcoholic potash. It is reconverted into ethyl phthalylidimalonate by the action of acids.

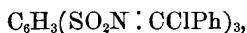
If phthalic chloride is added to a mixture of ether and ethyl sodium-malonate at the ordinary temperature, the chief product of the reaction is ethyl phthalylmalonate, but if half the chloride is slowly added to the warm mixture, and the product heated for some time before the remainder of the phthalic chloride is added, the chief product is ethyl phthaloxylidimalonate, a small quantity of ethyl phthalylidimalonate is also formed. By reversing the process, and adding the mixture of ether and ethyl sodium malonate to the phthalic chloride, a large yield of ethyl phthalylmalonate is obtained, together with half the weight of phthalylidimalonate, and $\frac{1}{10}$ th of phthaloxylidimalonate. Phthalic anhydride acts on ethyl sodium malonate, forming sodium phthalate, ethyl phthalylmalonate and ethyl malonate.

W. C. W.

Benzenetrisulphonic Acid. By C. L. JACKSON and J. F. WING (*Amer. Chem. J.*, **9**, 325—347. Compare Abstr., 1886, 623).—Senhofer prepared benzenetrisulphonic acid by heating benzene with phosphoric anhydride and fuming sulphuric acid; the authors in preparing potassium benzeneparadisulphonate also obtained benzenetrisulphonic acid; and its formation was proved to be due, during a second heating of the ingredients, to the action of potassium sulphate previously formed; a similar action possibly takes place in Claesson's method (heating a potassium sulphonate with sulphuryl chloride), and Neville and Winther's method (heating the acid sulphates of the amines). The potassium sulphate can be replaced by silver sulphate, and very imperfectly by aluminium sulphate, but not by zinc sulphate, and it therefore acts not as a dehydrating agent, but as a carrier of sulphuric acid.

Potassium benzenetrisulphonate, $\text{C}_6\text{H}_3(\text{SO}_3\text{K})_3 + 3\text{H}_2\text{O}$ [= 1 : 3 : 5], is easily prepared by heating 15 grams of potassium benzenemetadisulphonate with 18 grams of strong sulphuric acid, until the mass begins to get pasty, when it is dissolved in water and converted into the potassium salt by the usual methods; the yield amounts to 44 per cent. The preparation may be made from benzene itself, but the product is more difficult to purify owing to the formation of paradisulphonic compounds. The salt forms monoclinic plates or needles: $\beta = 68^{\circ} 38\frac{1}{2}'$; $a : b = 1 : 2.10$; 35.46 parts of the anhydrous salt are dissolved by 100 of water at 20° . Attempts to brominate or nitrate the acid were unsuccessful. *Benzenetrisulphonic chloride*, $\text{C}_6\text{H}_3(\text{SO}_2\text{Cl})_3$, is prepared by the usual methods; it melts at 184° and soon after sublimes slowly; it is slowly decomposed by boiling water,

and is best recrystallised from chloroform. *Ethyl benzenetrisulphonate*, $C_6H_3(SO_3Et)_3$, is readily obtained from the silver salt and ethyl iodide; other methods are not suitable. It melts at 147° , but is decomposed by long heating at lower temperatures. It crystallises readily from benzene, and is insoluble in water; it is decomposed by boiling with absolute alcohol, the free acid and ethyl ether being formed. *Benzenetrisulphonamide*, $C_6H_3(SO_2NH_2)_3$, is formed from the chloride by the action of aqueous ammonia. It may be crystallised from water or alcohol, and melts at $310-315^\circ$. The following salts are described, $C_6H_3(SO_2NHAg)_3$, $C_6H_3(SO_2NHHg\cdot OH)_3$, and $[C_6H_3(SO_2NH)_2]_2Hg$, both formed with difficulty, and $[C_6H_3(SO_3)_3]_2[Cu(NH_3)_4]_3$. Attempts to prepare the imide were not altogether successful. *Benzenetrisulphobenzoylamide*, $C_6H_3(SO_2NHBz)_3$, is obtained by acting with benzoic chloride on the sulphonamide at temperatures not above 140° . It is purified by crystallisation from alcohol, but shows no definite melting point, owing to its ready decomposition. It dissolves easily in alkalis, and forms salts such as $C_6H_3(SO_2NNaBz)_3$, and $[C_6H_3(SO_2NBz)_3]_3Ba_3 + 12H_2O$, both being uncrystallisable. When the benzoylamide is treated with phosphorus pentachloride, the substance



is formed, which by warming with aniline is converted into the compound $C_6H_3(SO_2N : CPh\cdot NPh)_3$, melting at 195° , and best crystallised from alcohol. *Benzenetrisulphanilide*, $C_6H_3(SO_2NHP)_3$, formed by the action of aniline on the sulphochloride; it crystallises well from alcohol, and melts at 237° .

The constitution of the benzenetrisulphonic acid here described is ascertained by fusion of the potassium salt with potassium cyanide and saponifying the nitrile formed, when the only product is trimesic acid; moreover, when the sulphochloride is heated with phosphorus pentachloride at 200° , it is converted into the symmetrical trichlorobenzene, hence $[(SO_3H)_3 = 1 : 3 : 5]$.

H. B.

Sulphonefluorescein. By I. REMSEN and C. W. HAYES (*Amer. Chem. J.*, 9, 372—379).—It has been previously shown (Abstr., 1885, 539), that when resorcinol is heated with orthosulphobenzoic acid, it yields a highly fluorescent substance. This is now shown to be one of a new class of compounds, the sulphonphthaleins.

Sulphonfluorescein, $O < \begin{smallmatrix} C_6H_3(OH) \\ C_6H_3(OH) \end{smallmatrix} > C < \begin{smallmatrix} C_6N_4 \\ -O- \end{smallmatrix} > SO_2 + 2H_2O$, is obtained when orthosulphobenzoic acid is fused with resorcinol at $175-185^\circ$ until the mass becomes pasty. The mass is crystallised from water, and the crystals washed with ether; they are pale straw-yellow, and probably monoclinic. It shows a feeble green fluorescence, much stronger in alkaline solution, is very soluble in water and alcohol, but dissolves only slowly in ether. It does not melt without decomposition. It has decided acid reactions, differing from fluorescein in that it decomposes carbonates. The barium, $(C_{19}H_{13}O_7S)_2Ba$, and calcium salts are described, as also a crystalline acetyl-derivative. When treated with bromine in acetic acid solution, it yields a dibromide, $C_{19}H_{10}Br_2O_6S$, and with sulphuric acid it yields an intensely fluorescent

acid. Nascent hydrogen reduces it to a colourless substance that re-oxidises in the air. H. B.

Diphthalic Acid. By C. GRAEBE and P. JUILLARD (*Annalen*, **242**, 214—257).—Pure diphthalic acid is a colourless substance which melts at 270—272°. The *methyl salt*, $C_{16}H_8O_6Me_2$, obtained by the action of methyl iodide on silver diphthalate, crystallises in plates of a lemon colour. It melts at 191—192°. The *ethyl salt* forms lemon-coloured needles, and melts at 154—155°. When hydrogen chloride is passed into warm ethyl alcohol containing diphthalic acid in solution and suspension, colourless plates are deposited of the composition $C_{16}H_{14}O_6$. The compound melts at 174°, and dissolves in alcohol, ether, and chloroform. If methyl alcohol is substituted for ethyl alcohol in the previous experiment, a crystalline compound is obtained which melts at 275°. After recrystallisation from phenol, it seems to have the composition $C_{16}H_{14}O_6$. These substances are decomposed by hydrochloric acid at 150°, yielding diphthalic acid and methyl or ethyl chloride.

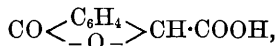
At 180°, hydroxylamine hydrochloride acts on diphthalic acid in presence of alcohol, forming a compound of the composition $C_{16}H_{18}N_2O_4$. This substance is also formed by heating at 100° in sealed tubes a mixture of hydroxylamine hydrochloride, alcohol, and diphthalic anhydride, but if the operation is carried on in an open vessel an ethereal salt is produced. The first compound crystallises in slender needles, melts at 285—286°, and dissolves in phenol.

The lactone of benzhydroltricarboxylic acid is obtained by dissolving diphthalic acid in a 4 per cent. solution of sodium hydroxide, and heating the solution at 110—115° for three minutes. When cold, the product is acidified with hydrochloric acid and the lactone is precipitated. It is soluble in chloroform and in alcohol. On boiling the alcoholic solution, carbonic anhydride escapes, and the lactone of benzhydroldicarboxylic acid is formed. On reduction with phosphorus and hydriodic acid at 170°, the lactone of benzhydroltricarboxylic acid is converted into *diphenylmethanetricarboxylic acid*,



This acid is soluble in hot water and crystallises with 1 mol. H_2O . It begins to decompose at its melting point, 218—220°, and at 250—270° it is completely converted into a red compound, $C_{16}H_8O_4$, which melts at 260°. This red substance is also formed by dissolving the acid in warm sulphuric acid and pouring the solution into water.

Benzhydroldicarboxylic acid, $OH \cdot CH(C_6H_4 \cdot COOH)_2$, is formed by heating diphthalic acid with a 50 per cent. solution of potassium hydroxide at 125—130° for five minutes. The lactonic acid,



dissolves freely in alcohol, ether, and chloroform; it melts at 203°. On oxidation, the alkaline solution yields benzophenonedicarboxylic acid, and the acid solution when treated with chromic acid yields the dilactone of the above acid. On reduction with hydriodic acid and

phosphorus, diphenylmethanedicarboxylic and dihydroanthracene-carboxylic acids are obtained.

If the lactone is sublimed, the sublimate melts at 171° , and has the same composition as the lactone.

The potassium and barium salts ($C_{15}H_{10}O_5Ba + H_2O$) of benzhydroldicarboxylic acid are amorphous. The ammonium salt of the lactone is crystalline. The following salts of the lactone are insoluble in water: $(C_{15}H_9O_4)_2Ba + 2\frac{1}{2}H_2O$, $(C_{15}H_9O_4)_2Cu + 3H_2O$, and $C_{15}H_9O_4Ag$. The methyl salt melts at $154-155^{\circ}$, and the ethyl salt at 99.5° . The amide, $C_{15}H_9O_3 \cdot NH_2$, crystallises in needles, and melts at $158-160^{\circ}$. The lactone unites with phenylhydrazine, forming the crystalline compound $C_{21}H_{16}N_2O_3$. It also forms a crystalline dinitro-derivative, $C_{15}H_9O_4(NO_2)_2$, melting between 270° and 280° . The ethyl salt, $C_{15}H_7O_4(NO_2)_2Et$, melts at $146-148^{\circ}$.

Benzophenonedicarboxylic acid, $CO(C_6H_4 \cdot COOH)_2$, is soluble in alcohol, ether, and acetic acid. It melts between 150° and 155° , losing a molecule of water, and forming the dilactone. The potassium and ammonium salts crystallise in needles, and are freely soluble in water. The copper salt is insoluble, and the silver salt sparingly soluble. The *barium* salt, $C_{16}H_8O_6Ba + 5H_2O$, forms prisms, which dissolve freely in hot, and sparingly in cold water. Anthraquinone is formed when the anhydrous barium salt is strongly heated. The methyl salt, $C_{15}H_8O_5Me_2$, melts at $85-86^{\circ}$, and the ethyl salt at $73-74^{\circ}$.

The dilactone of benzophenonedicarboxylic acid, $C\left(\begin{smallmatrix} C_6H_4 \\ -O- \end{smallmatrix} CO \right)_2$, is obtained in crystals when strong hydrochloric acid is added to a concentrated alcoholic solution of benzophenonedicarboxylic acid. It is soluble in benzene, chloroform, hot acetic acid, and hot alcohol. When reduced with zinc-dust and acetic acid, it is converted into the lactone of benzhydroldicarboxylic acid, and when reduced with hydriodic acid and phosphorus at 170° , it yields diphenylmethanedicarboxylic acid and a small quantity of dihydroanthracenecarboxylic acid. At 200° , if much phosphorus is used, the chief product is methylanthracene hexahydride. Fuming sulphuric acid converts the dilactone into anthraquinonesulphonic acid. The imide of benzophenonedicarboxylic acid is obtained on heating the ammonium salt of the acid, or by the action of ammonia on the dilactone; it forms colourless crystals, and melts at $251-252^{\circ}$. It is converted into the *di-imide*, $C_{15}H_{10}O_2N_2$, by treatment with alcoholic ammonia at 140° ; this is soluble in acetic acid, hot water, and hot alcohol. It crystallises in prisms, and melts at $284-286^{\circ}$. The acetoxime of benzophenonedicarboxylic acid forms colourless crystals, and melts at $213-214^{\circ}$. When the dilactone is treated with dilute alcohol and hydroxylamine hydrochloride at a gentle heat, the ethyl salt of the acetoxime is obtained; it melts at $146-149^{\circ}$.

Phenylhydrazine unites with benzophenonedicarboxylic acid, forming a crystalline compound of the composition $C_{21}H_{16}O_5N_2$, which melts at 155° , and loses 2 mols. H_2O , yielding the compound $C_{21}H_{14}O_4N_2$. This substance can also be prepared by slowly adding

phenylhydrazine to a warm alcoholic solution of the dilactone. It melts at 230°, and is soluble in hot alcohol.

Diphenylmethanedicarboxylic acid, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{COOH})_2$, melts at 254.5°, and at 280° yields a sublimate which consists of a mixture of anthraquinone and unaltered acid. The acid is soluble in alcohol and ether. It is oxidised by potassium permanganate to benzophenonedicarboxylic acid. Strong sulphuric acid at 100° converts it into α -anthranolcarboxylic acid. The barium salt, $\text{C}_{15}\text{H}_{10}\text{O}_4\text{Ba} + 6\text{H}_2\text{O}$, is crystalline. The methyl salt, $\text{C}_{15}\text{H}_{10}\text{O}_4\text{Me}_2$, is very soluble in alcohol, and melts at 43—44°.

α -*Anthranolcarboxylic acid* dissolves freely in alcohol and ether, and melts at 252—253°; when oxidised, it yields anthraquinonecarboxylic acid melting at 286°. α -*Dihydroanthracenecarboxylic acid*,

$\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CH}_2\end{smallmatrix}\rangle\text{C}_6\text{H}_3\cdot\text{COOH}$, crystallises in yellow prisms, and is soluble

in alcohol and ether. It melts at 209°, and on oxidation with potassium permanganate yields the anthraquinonecarboxylic acid which melts at 288°. α -*Methylantracene hexahydride* crystallises in plates, and dissolves freely in alcohol, ether, and chloroform. On oxidation with a mixture of chromic and acetic acids, it yields α -methylanthraquinone, crystallising in yellow needles, and melting at 152—154°.

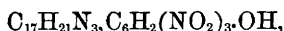
W. C. W.

Auramines. By W. FEHRMANN (*Ber.*, **20**, 2844—2862).—Commercial auramine is the hydrochloride of a base obtained by the action of ammonium chloride on tetramethyldiamidobenzophenone; the author, however, gives to the base itself the name auramine.

Tetramethyldiamidobenzophenone (this Journ., 1876, ii, 298) crystallises in silvery-white scales, melts at 172—172.5°, and is insoluble in water, very sparingly soluble in ether, soluble in alcohol and benzene. The *hydrochloride*, $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}\cdot 2\text{HCl}$, crystallises from alcohol in small, white, radially-grouped prisms, and decomposes in aqueous solution with separation of the base; the *platinochloride*, $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}\cdot \text{H}_2\text{PtCl}_6$, is a granular, yellow precipitate, sparingly soluble in water and alcohol; the *picrate*, $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}\cdot \text{C}_6\text{H}_3(\text{NO}_2)_3\text{OH}$, crystallises from alcohol in small, purple-red, radially-grouped prisms, melts at 156—157°, and is very sparingly soluble in hot water, soluble in alcohol.

Auramine hydrochloride (commercial auramine), $\text{C}_{17}\text{H}_{21}\text{N}_3\cdot \text{HCl} + \text{H}_2\text{O}$, is prepared by heating equal parts of tetramethyldiamidobenzophenone, ammonium chloride, and zinc chloride at 150—160° until the melt is almost completely soluble in water. It crystallises from water (at 60—70°), in beautiful, yellow scales, decomposes at 265—280°, without previous fusion, and is sparingly soluble in cold water, soluble in alcohol. Dilute mineral acids readily convert it into tetramethyldiamidobenzophenone even in the cold, and the same change is effected by boiling the aqueous solution. Cotton prepared with tannin is tinged a pure yellow by the dye, and the colour is little affected by acids. *Auramine*, $\text{NH} : \text{C}(\text{C}_6\text{H}_4\cdot \text{NMe}_2)_2$, crystallises from alcohol by spontaneous evaporation in citron-yellow scales, and is insoluble in water and ether, soluble in alcohol; the *platinochloride*, $(\text{C}_{17}\text{H}_{21}\text{N}_3)_2\cdot \text{H}_2\text{PtCl}_6$, separates from mixed aqueous

solutions of the constituents as a yellow, granular precipitate, insoluble in water, and sparingly soluble in alcohol; if, however, alcoholic solutions are employed, the chief product is the platinum-chloride of tetramethyldiamidobenzophenone; the *picrate*,



crystallises in slender, yellow scales, melts at $230\text{--}236^\circ$, and is insoluble in cold water, sparingly soluble in cold alcohol; the *oxalate*, $(\text{C}_{17}\text{H}_{21}\text{N}_3)_2, \text{H}_2\text{C}_2\text{O}_4$, crystallises in small, orange-yellow needles, melts at $193\text{--}194^\circ$, with the evolution of gas, and is sparingly soluble in water, soluble in warm alcohol.

Phenylauramine hydrochloride, $\text{C}_{23}\text{H}_{25}\text{N}_3, \text{HCl}$, is formed when auramine hydrochloride is heated with aniline at $175\text{--}180^\circ$ until ammonia ceases to be evolved, or when tetramethyldiamidobenzophenone is heated with aniline hydrochloride. It is a reddish, crystalline mass, which dissolves in water and alcohol, and gradually in aqueous solution, or more rapidly on treatment with mineral acids, decomposes into tetramethyldiamidobenzophenone and aniline. *Phenylauramine*, $\text{NPh} \cdot \text{C}(\text{C}_6\text{H}_4\text{NMe}_2)_2$, crystallises from alcohol in small, greyish-yellow, radially-grouped needles, decomposes at 80° into a solid and a liquid substance, and is insoluble in water and ether, soluble in alcohol; the *platinochloride*, $(\text{C}_{23}\text{H}_{25}\text{N}_3)_2, \text{H}_2\text{PtCl}_6$, and *picrate*, $\text{C}_{23}\text{H}_{25}\text{N}_3, \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, are flocculent and dissolve in alcohol.

Tolylauramine hydrochloride, obtained by heating auramine hydrochloride with paratoluidine at 160° , resembles the phenyl-derivative in its properties; the *platinochloride*, $(\text{C}_{24}\text{H}_{27}\text{N}_3)_2, \text{H}_2\text{PtCl}_6$, forms red flocks, soluble in alcohol.

Tolyleneauramine, $\text{C}_6\text{H}_3\text{Me} < \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} > \text{C}(\text{C}_6\text{H}_4\text{NMe}_2)_2$, is formed when auramine hydrochloride is heated with metaparatoluylenediamine at 160° , and the resulting hydrochloride is treated with ammonia. It crystallises from alcohol in small, brown scales, and in dilute acetic acid solution dyes cotton prepared with tannin a reddish-brown. In acetic acid solution, or more rapidly on treatment with dilute mineral acids, it is decomposed into tetramethyldiamidobenzophenone. The *hydrochloride* crystallises in very slender, small, brown needles, and decomposes very readily; the *platinochloride*, $\text{C}_{24}\text{H}_{28}\text{N}_4, \text{H}_2\text{PtCl}_6$, and the *picrate*, $\text{C}_{24}\text{H}_{28}\text{N}_4, 2\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, are soluble in alcohol.

Ethyleneauramine, $< \begin{smallmatrix} \text{CH}_2\text{NH} \\ \text{CH}_2\text{NH} \end{smallmatrix} > \text{C}(\text{C}_6\text{H}_4\text{NMe}_2)_2$, prepared in like manner from ethylenediamine, crystallises from alcohol in yellowish scales, is insoluble in water, soluble in alcohol, and decomposes into tetramethyldiamidobenzophenone in acetic acid solution, or on treatment with mineral acids. It dyes cotton prepared with tannin yellow with a shade of red. The *hydrochloride* forms yellow needles, and is very unstable; the *platinochloride*, $\text{C}_{19}\text{H}_{26}\text{N}_4, \text{H}_2\text{PtCl}_6$, and *picrate*, $\text{C}_{19}\text{H}_{26}\text{N}_4, 2\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, were also prepared.

If the auramines, instead of being heated with water, are dissolved in warm alcohol, and treated with hydrogen sulphide, an analogous decomposition occurs with the production of ammonia or the corresponding amine and tetramethyldiamidothiobenzophenone. The

latter crystallises in small, dark-red, flattened needles, and melts at about 164° , although by repeated crystallisation the melting point slowly rises, owing apparently to slight decomposition. When warmed with mineral acids, or when heated with water at 110 — 120° , it is decomposed into hydrogen sulphide and tetramethyldiamidobenzophenone. The *platinochloride*, $C_{17}H_{20}N_2S, H_2PtCl_6$ (compare Abstr., 1887, 816), forms violet-black flocks, insoluble in water and ether, sparingly soluble in alcohol, but readily soluble in excess of hydrochloric acid to a purple-red solution, which readily decomposes with the separation of platinum sulphide.

On treatment with carbon bisulphide in the cold, auramine is converted into a mixture of tetramethyldiamidothiobenzophenone and thiocyanic acid, whilst phenylauramine, when heated at 150° for five hours with carbon bisulphide, yields the thioketone and phenyl thiocarbimide.

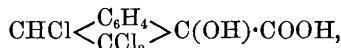
W. P. W.

Auramine. By C. GRAEBE (*Chem. Centr.*, 1887, 951, from *Monit. Sci.*, 1887, 601).—Auramine, first obtained by Kern and Caro, is prepared by heating tetramethyldiamidobenzophenone with ammonium and zinc chlorides. The free base is colourless, the hydrochloride, which has been introduced into commerce, forms golden-yellow leaflets, sparingly soluble in cold, readily in hot water.

V. H. V.

β -Naphthaquinone. By T. ZINCKE (*Ber.*, 20, 2890—2895; compare Abstr., 1887, 53).—*Trichlorodiketohydronaphthalene hydrate*, $C_6H_4 < \begin{smallmatrix} CO \cdot CO \\ CHCl \end{smallmatrix} > CCl_2 + 2H_2O$, is prepared by passing chlorine into glacial acetic acid containing β -naphthaquinone, filtering, and keeping the solution for two days in a closed vessel; water is then added, and the trichloride, which separates in thin, white needles, is crystallised from alcohol or glacial acetic acid. It forms large, lustrous, well-formed crystals, probably monoclinic, which melt at 112° with separation of water; at 180° , it becomes red and gives off hydrogen chloride. The anhydrous substance forms a tough, yellowish mass, which separates from benzene in highly coloured crystals melting at 128° . When warmed with methylamine in alcoholic solution, the compound $C_6H_4 < \begin{smallmatrix} CO \cdot C(OH) \\ C : NMe \end{smallmatrix} > CCl$ separates in intensely red scales of a metallic lustre, melting at 200° . Two other compounds, melting at 237° and 160° respectively, are formed.

Trichlorethylenephenyleneglycollic acid,



is formed when the trichloride is dissolved in dilute aqueous soda, and separates as an oil on adding an acid. The *methyl salt* crystallises in colourless, lustrous, monoclinic crystals melting at 150° . The *acetyl-derivative* crystallises in small needles which melt at 114 — 116° .

Phenylenetrichlorethylene ketone, $CHCl < \begin{smallmatrix} C_6H_4 \\ CCl_2 \end{smallmatrix} > CO$, is prepared by oxidising the above hydroxy-acid with dilute chromic acid, and sepa-

rates as an oil, which gradually solidifies. It crystallises from alcohol in thick pointed needles, having a peculiar odour resembling that of benzophenone; it is readily soluble, melts at $58-59^{\circ}$, and distils slowly with steam.

Orthodichlorovinylbenzoic acid, $C_2HCl_2 \cdot C_6H_4 \cdot COOH$, is obtained by dissolving the trichloroketone in an alkali and adding acid. It crystallises from dilute alcohol in long, slender needles melting at $120-121^{\circ}$. It is reduced by sodium amalgam to orthoethylbenzoic acid melting at 68° . The *methyle salt* crystallises in thick needles which melt at 47° .
N. H. M.

Hydro-derivatives of Aromatic Bases. By E. BAMBERGER (*Ber.*, 20, 2915—2917).— β -Tetrahydronaphthylamine, $C_{10}H_{11} \cdot NH_2$, prepared by the reduction of β -naphthylamine with sodium, is a very strong base, capable of displacing ammonia from its salts. It forms stable, crystalline salts with carbonic anhydride, and by carbon bisulphide is converted with explosive violence into tetrahydronaphthylamine tetrahydronaphthylsulphocarbamate. The isomeric α -derivative is a feeble base, which does not react alkaline or yield a carbonate. It reacts like a normal amine with nitrous acid.

It is suggested that the hydro-derivatives of the aromatic bases are related to bases of the camphor-group, and that tetrahydro- β -naphthylamine and Leuckart and Bach's bornylamine (*Abstr.*, 1887, 376) are similarly constituted.
N. H. M.

Orthamidazo- and Hydrazimido-compounds. By T. ZINCKE and A. T. LAWSON (*Ber.*, 20, 2896—2903; compare *Abstr.*, 1886, 795, and 1887, 731).—Benzeneazo- β -naphthylamine is a much feebler base than orthamidazotoluene; the salts are readily decomposed by alcohol and water. The *hydrochloride* crystallises in yellowish needles; the *sulphate*, $NH_2 \cdot C_{10}H_6 \cdot N_2Ph \cdot H_2SO_4$, forms brownish-yellow needles. The *diazochloride* is prepared by dissolving 1 part of the azo-compound in 15 parts of hot glacial acetic acid and adding 3 parts of strong hydrochloric acid; cold nitrous acid is then passed through, and the whole kept until a clear, dark-red solution is obtained. The *platinochloride*, $(N_2Cl \cdot C_{10}H_6 \cdot N_2Ph)_2PtCl_4$, forms small, yellow, sparingly soluble needles. The *diazosulphate* is less soluble than the chloride; the *perbromide*, $N_2Br_3 \cdot C_{10}H_6 \cdot N_2Ph$, forms small, red needles. When the solution of the diazochloride in acetic acid is diluted with water, nitrogen is evolved, and benzeneazo- β -naphthol is formed. When the well-cooled acetic acid solution of the diazochloride is treated with stannous chloride, heated on a water-bath, and filtered, the *diazohydride*, $N_2H \cdot C_{10}H_6 \cdot N_2Ph$, is obtained; this crystallises from benzene or alcohol in colourless, lustrous needles, melting at $204-205^{\circ}$. The *acetyl-derivative*, $N_2Ac \cdot C_{10}H_6 \cdot N_2Ph$, crystallises from alcohol in lustrous needles which melt at $137-139^{\circ}$.

β -Amidazonaphthalene hydrochloride, $C_{10}H_7 \cdot N_2 \cdot C_{10}H_6 \cdot NH_2 \cdot HCl$, forms small, brownish-yellow needles; the *sulphate* crystallises in brownish-yellow needles. The *diazochloride* is decomposed by water, with formation of β -hydroxyazonaphthalene (Nietzki and Goll, *Abstr.*, 1886, 714) and evolution of nitrogen. The *diazohydride*, $N_2H \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_7$,

crystallises in white needles melting at 202—204°, is readily soluble in hot alcohol and hot glacial acetic acid, sparingly soluble in benzene.

N. H. M.

Sulphonation of Acetonaphthalide. By M. LANGE (*Ber.*, 20, 2940—2941).— α -Acetonaphthalide is sulphonated by adding it in fine powder to fuming sulphuric acid containing 20 per cent. of anhydride. The sulphonic acid is unstable, and loses the acetyl-group when boiled with alkalis or acids.

α -Naphthylaminesulphonic acid is obtained by treating the solution of acetonaphthalidesulphonic acid in sulphuric acid with twice the bulk of water. It crystallises in needles much more soluble than naphthionic acid; the salts are also much more soluble than those of the naphthionic acid. The solution shows a green fluorescence. The *benzylidene compound* crystallises in long needles. When the acid is diazotised and boiled with alcohol, a naphthalenesulphonic acid is formed, which yields α -naphthol when fused with potash.

N. H. M.

α -Naphthalenedisulphonic Acid. By A. WEINBERG (*Ber.*, 20, 2906—2911).— α -Naphthalenedisulphonic acid is converted by the action of soda into a new β -naphtholsulphonic acid. This, when heated with ammonia, is converted into β -naphthylaminesulphonic acid, from which β -naphthalenemonosulphonic acid was obtained by means of the diazo-compound. Assuming that β -naphthalenedisulphonic acid has the constitution [2 : 3'], the constitution of α -naphthalenedisulphonic acid would be [2 : 2'].

$\beta\beta$ -Naphtholsulphonic acid, [2 : 2'] (known as naphtholsulphonic acid F.), is prepared by heating sodium naphthalenedisulphonate (100 grams), soda (30 grams), and water (300 c.c.), for 12 hours at 250°. The product is recrystallised and converted into the barium salt; the free acid is recrystallised from strong hydrochloric acid, from which it separates in needles which melt, when dried, at 89°. It is readily soluble in water and alcohol, insoluble in ether and benzene. When the sodium salt is heated with phosphorus pentachloride (3 parts) at 165°, chloronaphthol phosphate melting at 215° is formed as chief product, together with a naphthalene dichloride, which crystallises from methyl alcohol in rhombic plates which melt at 114°. *Sodium naphtholsulphonate* crystallises with 2½ mols. H₂O in large plates; the *potassium salt* with 1 mol. H₂O forms rhombic crystals. Both salts are readily soluble in water. The *magnesium salt* crystallises in plates with 5½ mols. H₂O; the *barium salt* is sparingly soluble, but more soluble than the barium salt of Schaeffer's β -naphtholsulphonic acid. Nitrous acid converts the sulphonic acid into a *nitroso-compound*; the *sodium salt* crystallises with 2 mols. H₂O in golden needles.

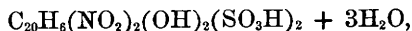
Naphthylaminesulphonic acid [2 : 2'] (F.), is obtained by the action of ammonia on the naphtholsulphonic acid; it dissolves in 350 parts of boiling water. The *barium salt* with 5 mols. H₂O crystallises in well-formed needles; the *magnesium salt* crystallises with 5½ mols. H₂O.

Bayer and Duisberg's β -naphthylamine- δ -sulphonic acid (*Abstr.*, 1887, 732) is not identical with the acid [2 : 2'], but is a mixture.

β -Naphthol- δ -disulphonic acid, prepared from 2 : 2' naphtholsulphonic acid, yields with diazobenzene a crystalline orange dye, and with α -diazonaphthalene a Bordeaux, which crystallises in violet plates. The sodium salt is readily soluble in water, from which it is precipitated by alcohol as a yellow powder; the barium salt with $2\frac{1}{2}$ mols. H_2O crystallises in prisms soluble in 180 parts of boiling water. The solutions of the salts show a green fluorescence.

N. H. M.

Derivatives of Dinaphthyl. By P. JULIUS (*Chem. Ind.*, 10, 97—99).—The author has modified Dianin's method of preparing α - and β -dinaphthol. He proposes to treat an aqueous solution of sodium naphthoxide with a mixture of ferric chloride and hydrochloric acid, whereby the naphthol, which separates in a finely-divided state, is oxidised into dinaphthol as soon as it is brought into contact with ferric chloride. The following reaction occurs:— $2C_{10}H_7\cdot OH + Fe_2Cl_6 = C_{20}H_{12}(OH)_2 + Fe_2Cl_4 + 2HCl$. In practice it is necessary to use 2 mols. of hydrochloric acid to 1 mol. of ferric chloride. α -Dinaphthol thus prepared forms a white, crystalline powder melting at 296—299°. β -Dinaphthol forms pale-yellow, glistening needles melting at 217°. The yields of α - and β -dinaphthols are 70 to 75 and 85 to 95 per cent. respectively as compared with theory. On treating β -dinaphthol with sulphuric acid, and saturating the resulting sulphonic acid with barium carbonate, the barium salt of β -dinaphthol-disulphonic acid, $C_{20}H_{10}(OH)_2(SO_3)_2Ba + 6H_2O$, separates, whilst the filtrate contains the barium salt of β -dinaphtholtetrasulphonic acid, $C_{20}H_8(OH)_2(SO_3)_4Ba$. Dinitro- β -dinaphtholdisulphonic acid,



is obtained by treating the barium salt of the disulphonic acid with nitric acid. It crystallises from alcohol in yellow, silky needles. β -Dinaphthol does not combine with diazo-compounds; α -dinaphthol, however, does so readily, giving rise to a series of dyes. D. B.

Diamidopyrene. By R. JAHODA (*Monatsh.*, 8, 449—451).—The hydrochloride of this base is obtained by the reduction of dinitropyrene (Goldschmidt, *Abstr.*, 1881, 206); it forms white needles. Diamidopyrene, $C_{16}H_8(NH_2)_2$, is very unstable in the free state, resinifying very rapidly. The sulphate forms a white substance, insoluble in water and alcohol, and decomposes when heated. L. T. T.

Diterebenthyl. By A. RENARD (*Compt. rend.*, 105, 865—868).—The resin oils obtained by the destructive distillation of colophony consist mainly of a hydrocarbon which boils above 300°, and can be isolated by successive washings with sodium hydroxide solution, and then with water, followed by fractionation. The liquid thus obtained has the composition $C_{20}H_{30}$, and boils at 343—346°; sp. gr. at 18° = 0.9688; vapour-density 9.6; rotatory power for $[\alpha]_D = +59^\circ$; refractive index 1.53. It seems to be diterebenthyl, formed by the condensation of 2 molecules of terebenthene with elimination of H_2O . When exposed to air in thin layers for five days, it absorbs about one-tenth of its weight of oxygen and forms a varnish. Chromic anhydride in

boiling acetic acid oxidises the hydrocarbon to carbonic oxide and carbonic anhydride. Potassium permanganate in aqueous solution converts it into carbonic anhydride and formic, acetic, and propionic acids.

When the hydrocarbon is poured gradually into well-cooled, fuming nitric acid, there is no evolution of gases, and on adding water a trinitro-derivative, $C_{20}H_{27}(NO_2)_3$, separates out. When dried in a vacuum, it forms a yellow powder soluble in alcohol and ether. If the ethereal solution of the hydrocarbon is treated with a current of hydrogen chloride, the compound $2C_{20}H_{30}, HCl$ is obtained. Bromine acts violently, but in solution in carbon bisulphide it yields the dibromide $C_{20}H_{30}Br_2$, and when the carbon bisulphide evaporates, the bromine-derivative decomposes with evolution of hydrogen bromide. The direct action of bromine on the hydrocarbon in presence of water yields the hexabromo-derivative $C_{20}H_{24}Br_6$, a dark-brown, amorphous solid, which melts below 100° , and is soluble in alcohol and ether.

Ordinary concentrated sulphuric acid converts diterebenthyl into a sulphonic acid, which is isolated by agitating with water and light petroleum. The liquid separates into three layers, the lower of which is dilute sulphuric acid, the middle the sulphonic acid, and the upper layer a solution of the unaltered hydrocarbon in the light petroleum, which does not dissolve the sulphonic acid. A certain quantity of a new hydrocarbon is formed, which is not attacked by acids. The sulphonic acid is converted into the ammonium salt, which is precipitated by adding sodium chloride to the solution. The sulphonic acid, $C_{20}H_{29}SO_3H$, is obtained by decomposing the ammonium salt with sulphuric acid and extracting with benzene. It is a dark-brown mass, soluble in water, alcohol, ether, and benzene, but insoluble in light petroleum. Its solutions are highly fluorescent, and are brown by transmitted light, green by reflected light. It decomposes carbonates of the alkalis and alkaline earths. The free acid is precipitated from its aqueous solution by sodium chloride, sulphuric acid, sodium sulphate, and calcium chloride.

The ammonium salt is soluble in water, forming fluorescent solutions. The barium, calcium, copper, and lead salts, which can be obtained by double decomposition, are all insoluble in water. They all dissolve in alcohol, ether, and benzene, and burn with a smoky flame.

C. H. B.

Bitter Principle of Calamus Root. By H. THOMS (*Annalen*, **242**, 257—260).—The author states that the reason Geuther (Abstr., 1887, 972) failed to obtain acorine and acoretine from calamus root is because he did not use the original process described by the author (Abstr., 1886, 895), and consequently obtained different results.

W. C. W.

Bitter Principle of Calamus Root. By A. GEUTHER (*Annalen*, **242**, 260—264).—A reply to the above.

Cubebin. By C. POMERANZ (*Monatsh.*, **8**, 466—470).—The author is investigating this compound from *Piper cubeba*, the formula of which was proved by Weidel to be $C_{10}H_{10}O_3$. Attempts to eliminate

possible alkyl-groups by the action of hydrogen chloride or iodide proved unavailing, as the substance always carbonised. When oxidised with permanganate, it yielded piperonylic acid, $C_8H_6O_4$. When treated with acetic anhydride, no aceto-derivative is formed, but an ether, $(C_{10}H_{10}O_2)_2O$, which crystallises in needles, is soluble in alcohol, and melts at 78° .

From these results, the author concludes that cubebín (i) is a derivative of a methylene ether of pyrocatechol; (ii) contains a side-chain, C_3H_5O , yielding carboxyl on oxidation; and (iii) contains this side-chain in the same position relatively to the two etheric oxygen-atoms as the carboxyl in protocatechuic acid stands to the two hydroxyls.

L. T. T.

Brominated Quinolines. By A. CLAUS and V. TORNIER (*Ber.*, **20**, 2872—2882).— γ -Bromoquinoline (Claus and Collischonn, *Abstr.*, 1887, 158) boils at 274 — 276° (uncorr.; not 273 — 274°), solidifies when cooled to below 0° and melts at 12 — 13° . The *oxalate* crystallises in stellate groups of prisms, melting at 107° (uncorr.). The *picrate* forms a loose, bright yellow precipitate, consisting of slender needles; it melts at 190° . The *ethobromide*, C_9NH_5Br , $EtBr$, is obtained by heating the base with ethyl bromide and absolute alcohol at 100° for some hours; it separates on cooling in lemon-coloured needles with 2 mols. $EtOH$, and melts at 216° (uncorr.). γ -Bromoquinoline dibromide hydrobromide is obtained when bromine is added to a solution of γ -bromoquinoline hydrobromide in chloroform, as a cinnabar-coloured mass of crystals, melting at 76° with decomposition; it was not analysed. When the hydrobromide is heated at about 200° , a new dibromoquinoline is obtained, together with its hydrobromide. The new base crystallises from alcohol in colourless, lustrous needles, which melt at 166° (uncorr.).

Parabromoquinoline is best purified by boiling with chromic acid. It is an almost colourless liquid which boils at 178° (uncorr.), solidifies when cooled to below 0° , and melts at 18 — 19° (uncorr.) When oxidised with potassium permanganate, it yields only quinolinic acid [$(COOH)_2 = 2 : 3$]. The *hydrobromide* forms colourless needles, which soon become red, and melt at about 256° . The hydrochloride (with 1 mol. H_2O) melts at 213° (uncorr.). The *nitrate* forms needles melting at 182° ; the *sulphate* crystallises (with 1 mol. H_2O) in small plates melting when dry at 176° ; the *chromate* forms small, yellow needles melting at 179° ; the *oxalate*, melting at 62° , the *picrate*, melting at 216 — 217° , and the *ethobromide*, melting at 230° (uncorr.), are also described. Parabromoquinoline dibromide hydrobromide is a very unstable, orange-red substance, which melts at 70° , and when heated at 200° yields dibromoquinoline, melting at 125 — 126° (Ia Coste, *Ber.*, **14**, 925; Claus and Küttner, *Abstr.*, 1887, 278).

Orthobromoquinoline, prepared from orthobromaniline and purified by chromic acid, forms a colourless oil boiling at 300 — 304° (uncorr.). The *hydrochloride*, C_9NH_5Br , $HCl + H_2O$, melts with decomposition at 166° ; the *platinochloride* crystallises from alcohol in small, bright yellow needles; the *nitrate* melts at 90° ; the dichromate begins to decompose at 100° , and melts at 168° .

Orthobromoquinoline dibromide hydrobromide forms orange-red

crystals, melting at 90° with decomposition; when heated at 200° , a new *dibromoquinoline* is formed, which sublimes in colourless, lustrous needles melting at 90° (uncorr.).

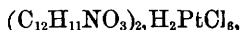
Metabromaniline yields a mixture of two isomeric metabromoquinolines which are best separated by means of the nitrates.

Metabromoquinoline, C_9NH_6Br , is an almost colourless oil, which boils at 280° (uncorr.), and does not solidify at -4° . The *hydrochloride* (with 1 mol. H_2O) is readily soluble in water, and melts at 225° with decomposition; the *platinochloride* is a yellow, very sparingly soluble substance; the *nitrate* is readily soluble in water, and melts at 165° (uncorr.); the *dichromate* forms reddish-yellow needles, melting at 190° with previous decomposition; the *ethobromide* melts at 290° (uncorr.). *Metabromoquinoline dibromide hydrobromide* is an orange-red crystalline substance, melting at 107° (uncorr.); when heated at 200° , it yields a *dibromoquinoline* which crystallises in prisms melting at 119° (uncorr.).

Anabromoquinoline is crystalline, melts at 32° and boils at 290° (uncorr.). The *hydrochloride* (with 1 mol. H_2O) forms small branched crystals, very readily soluble in water; it melts at 213° . The *nitrate* is much more sparingly soluble in water than its isomeride, and separates in concentrically-grouped needles melting at 199° (uncorr.). The *ethobromide* crystallises from alcohol in colourless, lustrous needles melting at 214° . *Anabromoquinoline dibromide hydrobromide* forms light yellow crystals, which melt at $106-107^\circ$ (uncorr.) with decomposition; when heated at 200° , *dibromoquinoline*, melting at 108° (uncorr.), is obtained. This crystallises in small, colourless needles.

N. H. M.

Ethyl Hydroxyquinoline Carbonate. By E. LIPPMANN (*Monatsh.*, **8**, 439—441).—When ethyl chloroformate and hydroxyquinoline are heated together, *ethyl hydroxyquinoline carbonate*, $C_9NH_6 \cdot O \cdot COOEt$, is formed. This crystallises in prisms, is soluble in boiling alcohol, chloroform, and ether, melts at 105° , and gives no coloration with ferrous sulphate or ferric chloride. The *platinochloride*,



crystallises in orange needles.

This ethyl salt when heated with caustic soda yields alcohol, hydroxyquinoline, and sodium carbonate; with strong hydrochloric acid at 140° , it yields ethyl chloride, carbonic anhydride, and hydroxyquinoline. It is thus a carbonate and not a carboxylic acid, and is not converted into the latter even by heating at 200° .

L. T. T.

Pyrenoline. By R. JAHODA (*Monatsh.*, **8**, 442—448).—Amidopyrene hydrochloride (Abstr., 1881, 206) was treated by Skraup's reaction with glycerol and sulphuric acid, when *pyrenoline*, $C_{15}NH_{11}$, was formed. This substance forms yellow scales soluble in boiling alcohol, and a dilute solution shows a strong green fluorescence. It is also soluble in benzene, ether, and chloroform. It melts at $152-153^\circ$. The *hydrochloride* forms orange, microscopic needles melting at 270° ; the *sulphate* pale red, hygroscopic needles melting at 246° ; the

platinochloride a red precipitate, still solid at 290° ; the *methiodide* dark red, microscopic needles melting at 212° , and soluble in alcohol; and the *picrate* yellow, microscopic needles, which decompose at 260° . The latter compound is well suited for the purification of the base.

When oxidised with permanganate, an acid is formed, but has not yet been isolated. L. T. T.

Action of Sulphuric Acid on Morphine and Bibasic Acids.

By P. CHASTAING and E. BARILLOT (*Compt. rend.*, **105**, 941—943, 1012—1014).—When morphine is dissolved in excess of dilute sulphuric acid, and the solution evaporated until white fumes are given off, sulphomorphide, a substance of variable composition which gives brown products with alkalis, is formed. If, however, morphine is heated with concentrated sulphuric acid at 120° , diluted with water, treated with alkalis for a very short time and then neutralised, it yields a slightly soluble compound of the composition $C_{14}H_{17}NO_4$. It always contains some sulphur in the form of sulphuryl, which is removed by strong alkalis, the compound being decomposed at the same time.

If morphine, 1 part, oxalic acid, 2 parts, and sulphuric acid, 1.5 part, are heated together at 115 — 120° for some hours, cooled and mixed with a large excess of water, a yellowish-white compound of the composition $C_{14}H_{17}NO_4$ or $C_{28}H_{34}N_2O_8$ is obtained. Malonic acid under similar conditions yields the compound $C_{30}H_{38}N_2O_{10}$, and succinic acid the compound $C_{32}H_{42}N_2O_{12}$. These compounds differ by $2CH_2O$. They are white, non-crystallisable substances which become greenish when exposed to air and light. They are insoluble in most neutral solvents, but are slightly soluble in cold water, more soluble in hot water. They behave like polyhydric phenols, and when mixed with alkalis oxidise on exposure to the air, forming red solutions. When these solutions are acidified, they deposit a deep blue flocculent precipitate soluble in ether, forming a violet-red solution, and in chloroform forming a blue solution, both of which deposit blue crystals of the composition $C_{28}H_{22}N_2O_4$ on evaporation.

The same compound, *morphine-blue*, is obtained with all three of the acids above-mentioned. At 100° , it contains 1 mol. H_2O , which is expelled at 120 — 125° . Each of the products from the bibasic acids absorbs 2 mols. of oxygen in alkaline solution, and forms 1 mol. of morphine-blue. This compound crystallises in slightly oblique prisms with a square base, which are red by transmitted light and blue by reflected light. They have no action on polarised light and melt to a blue liquid at a very high temperature. They are insoluble in water, slightly soluble in alcohol, and very soluble in ether, forming a solution which is red by transmitted light, and violet-red by reflected light. It also dissolves in chloroform, and alkalis remove the compound from both the ethereal and the chloroform solution, forming blue solutions. The compound in fact combines with alkalis to form salts which are somewhat stable when exposed to air. C. H. B.

Cinchonamine. By C. FRIEDEL (*Compt. rend.*, **105**, 985—987).—The crystals examined were obtained by Arnaud by gradually cool-

ing an alcoholic solution. They formed hexagonal prisms terminated by rhombohedral faces, the faces of the prisms being tangent to the edges of the rhombohedron. Sometimes the latter is modified by other faces. Optical examination shows, however, that the rhombohedral form is only apparent, and the crystals really consist of three rhombic sections macle along the faces m , and the faces which seem to be those of the fundamental rhombohedron are really the faces a' . The fundamental form is a rhombic prism, in which $mm = 60^\circ$, and $b : h = 1.6157$. The other angles were found to be $a'm = 47^\circ 39'$; $a'p = 51^\circ 4'$ (calc.), $e_3a' = 42^\circ 21'$ (calc.), $e_3p = 31^\circ 45'$ (calc.), $a'x = 53^\circ 29'$ (calc. $53^\circ 25'$) $xp = 68^\circ 10'$ (calc.); $xm = 36^\circ 42'$.

In two adjacent sections of the macle, $a'a' = 84^\circ 42'$. There is no outward sign of the structure, the faces e_3 and x being perfectly united, but the macles are not always regular, especially in the larger crystals. The crystals do not become uniaxial at a higher temperature
C. H. P.

Alkaloid from *Solanum Grandiflora*. By D. FREIRE (*Compt. rend.*, 105, 1074—1076).—The so-called "Wolf Fruit" of Brazil is the fruit of *Solanum grandiflora*, var. *pulverulentum*. Externally it is green, but the sarcocarp is white, somewhat thick, and has a bitter and disagreeable taste. It was treated with water and calcium hydroxide, evaporated to dryness on the water-bath, and the residue extracted with absolute alcohol and the solution filtered. The liquid was then concentrated to a small bulk, resinous matter being removed as it separated. After cooling, the semi-solid residue was treated with dilute hydrochloric acid, which dissolved the alkaloid but left the resinous matter undissolved. The acid solution was decolorised by animal charcoal, precipitated with ammonia, and the precipitate washed with water and dried over sulphuric acid.

The alkaloid thus obtained is a white substance with a very bitter taste, insoluble in water but soluble in alkalis and dilute acids. When heated with potassium hydroxide, it gives off ammonia, and its solution gives the usual reactions for alkaloids. With platinum tetrachloride, it gives a yellow precipitate; mercuric potassium iodide, a yellow precipitate; tannin, a turbidity; ammonia, a white precipitate; concentrated sulphuric acid, an egg-yellow colour changing to red; with sulphuric acid and manganese dioxide, a yellow colour becoming first green and then violet; concentrated nitric acid, a purplish-red colour. The molecular weight as determined by means of the platinum compound is 236.4.

The author proposes to call this alkaloid *grandiflorine*. It is an energetic poison, and the fruit itself kills sheep which eat it, hence its name.
C. H. B.

Trigonelline. By E. JAHNS (*Ber.*, 20, 2840—2843).—Trigonelline (*Abstr.*, 1886, 85), when heated at 120° with an aqueous solution of barium hydroxide saturated at the boiling point, yields the whole of its nitrogen as methylamine, and when heated with excess of hydrochloric acid (sp. gr. = 1.2) at 260 — 270° is converted into nicotinic acid and a combustible gas burning with a green flame, probably

methyl chloride. On these grounds, trigonelline is regarded as identical with the methylbetaine of nicotinic acid, and a comparison of the properties of the two substances shows this to be the case.

W. P. W.

Alkaloids extracted from the Bark of the Xanthoxylon Senegalense. By GIACOSA and MONARI (*Gazzetta*, 17, 362—367).—On extracting the bark of the *Xanthoxylon senegalense* (artar-root) with petroleum, an oil is obtained, from which a crystalline substance separates; this contains no nitrogen, and when purified has a white micaceous appearance, melts at 120—125°, and gives a purple-red coloration with chloroform and sulphuric acid. It is probably a pseudocholesterin, but sufficient material was not at hand for a more complete investigation. The bark, after treatment with petroleum, gives on prolonged boiling with alcohol a brownish extract, from which, on addition of alkali, a yellowish solid is obtained. This consists of two alkaloids, one of which is amorphous and insoluble in hot water, the other crystalline and soluble. The former was not further examined; the latter forms a *hydrochloride*, crystallising in minute needles or prisms, soluble in cold water, and of intensely bitter taste. The *nitrate* crystallises in needles melting at 215—220°; the *platinochloride* forms sparingly soluble yellowish prisms. The insoluble alkaloid produces muscular irritation with coagulation of myosin, and physiological disturbances analogous to those observed with veratrine. The compounds were not analysed.

V. H. V.

Formation of Peptone. By A. CLERMONT (*Compt. rend.*, 105, 1022—1023).—20 grams of chopped meat is mixed with 30 grams of water and 0.5 gram of sulphuric acid, and heated in sealed tubes at 180° for six hours. The products are gases and a slightly brown liquid, which is easily filtered. When evaporated to dryness, ammoniacal vapours are given off, and the residue dissolves readily in water. The solution is not affected by boiling, nor by hydrochloric, nitric, or acetic acids, but it is precipitated by 4 vols. alcohol of 90°, or by tannin, mercuric chloride, or platinic chloride. 4 grams of peptone are obtained from 20 grams of fresh meat. When heated with water without any acid, the meat is converted into syntonin, which is readily converted into peptone by pepsin at 35° in a slightly acid solution.

C. H. B.

Mucin of the Submaxillary Gland. By O. HAMMARSTEN (*Zeit. physiol. Chem.* 12, 163—195).—Obolensky (*Pflüger's Archiv*, 4, 336) and Landwehr (*Zeit. physiol. Chem.*, 5, 371) have both made analyses of submaxillary mucin, but their method of preparing the mucin was faulty. In the present research, the following method was first employed: the glands were extracted with water, the extract filtered, and freed from microscopic elements by centrifugalising; acetic acid was used to precipitate the mucin from this solution; the precipitate had a stringy character. Attempts were then made to wash this precipitate free from proteids by water acidified with acetic acid, the precipitate being repeatedly well kneaded with the acidified water; this was found to be exceedingly difficult. The mucin was redis-

solved in faintly alkaline water, and reprecipitated by acetic acid several times, but there was always the same difficulty in freeing it from proteids. This was found to be due to the presence in the gland extract of a proteid which is precipitable by acetic acid, and which is with difficulty soluble in excess of that reagent. It belongs to the class of proteids to which the name nucleo-albumin has been given. The older method of extracting the mucin from the glands with a weak alkali was not used, because it was found that sub-maxillary mucin is readily decomposed by this treatment. The nucleo-albumin contains 17 per cent. of nitrogen; and it was admixture with this substance that gave in Landwehr's analyses the somewhat higher percentage of nitrogen than was found subsequently in the present research. The new method ultimately adopted for the preparation of the mucin was as follows: the clear watery extract was acidified with hydrochloric acid until the percentage of the latter reached 0.1—0.15; the mucin which was first precipitated was redissolved when the acid present reached the percentage mentioned. The mixture was then diluted with three to five times its bulk of distilled water; by this means the mucin was precipitated, and the nucleo-albumin remained in solution. This process was repeated several times, until ultimately the mucin was obtained pure. Repeated precipitation and re-solution by this method does not alter the physical properties of the precipitate, which occurs in sticky, yellowish strings, nor does it alter its chemical properties or its elementary composition. This is in contrast with what occurs with dilute alkalis; a 0.1 per cent. solution of sodium hydroxide, or saturated or half saturated lime-water dissolves the mucin; but when precipitated by acetic acid its stringy character is lost, and the precipitate is flocculent; ammonia is given off in small quantities, and the percentage of nitrogen in the precipitate increases, the precipitate probably consisting of acid albumin.

The mucin prepared in the manner described was washed with water by decantation; when free from acid, it becomes white in colour, but becomes again brownish-yellow on the addition of acetic acid; it was then washed with alcohol and ether, and dried. Elementary analysis of seven preparations gave the following average results in percentages:—C, 48.84; H, 6.8; N, 12.32; S, 0.843; ash, 0.35. Previous statements as to the absence of sulphur in mucin appear to be incorrect. The extremely small quantity of phosphorus found might have been contained in the ash. The percentage composition corresponds closely with that obtained by Loebisch (*Abstr.*, 1886, 166), for tendon mucin. Mucin prepared in this way was found to be acid in reaction; this cannot be from union with the acid during its preparation, as the quantity of chlorine found by analysis was so excessively small; but mucin is probably itself of the nature of an acid. A neutral solution of mucin in 8 per cent. sodium chloride solution does not coagulate on heating, and even after adding acetic acid it only becomes slightly cloudy.

Alcohol precipitates mucin from a neutral solution; the precipitate is soluble in water, unless sodium chloride is present, in which case the precipitate is very insoluble. Mineral acids in small quantities pre-

precipitate mucin, and the precipitate is soluble in excess. Copper sulphate and ferric chloride, mercuric chloride, lead acetate, potassium dichromate, and potassium alum, all give slimy, gelatinous precipitates. Potassio-mercuric iodide gives no precipitate. Saturation with magnesium sulphate or sodium chloride precipitates mucin; Millon's, Adamkiewicz's, and the xanthoproteic reactions are all given by mucin. By heating with dilute mineral acids, a reducing substance is obtained. Potassium ferrocyanide gives no precipitate, or only a cloudiness in a solution of mucin in dilute hydrochloric acid. A sodium chloride solution can be pretty strongly acidified by acetic acid before precipitation occurs; and potassium ferrocyanide added to such a mixture produces no precipitate. Tannic acid in small quantities causes the liquid to become slimy and thick, and in excess causes precipitation. Of the varieties of mucin hitherto described, this approaches nearest to tendon mucin, but it differs from that in its solubility in dilute hydrochloric acid, and its behaviour to weak alkalis.

W. D. H.

The Mucin of Bile. By L. PAJKULL (*Zeit. physiol. Chem.*, **12**, 196—210).—Landwehr (*Zeit. physiol. Chem.*, **8**, 114) was the first to point out that the slimy substance in bile is not true mucin; he considered it to be a mixture of globulin with bile salts. An examination of his analytical results shows that there is some difficulty in accepting this view; for instance, the percentage of nitrogen in bile-mucin is 13·8; in paraglobulin, 15·85; and in glycocholic acid 2·5; there must therefore be 15·4 per cent. of glycocholic acid in the mixture called bile-mucin. The percentage of carbon on this calculation ought to be 55·01, but it is only 53·09. Moreover, although Landwehr states that a mixture of sodium glycocholate with serum-globulin has the physical characters of bile-mucin, it was found in this research that a mixture of globulin with bile deprived of its so-called mucin did not produce the characteristic sliminess of normal bile. The usual method of preparing mucin is not applicable to bile, as the bile-mucin is slightly soluble in excess of acetic acid. By dialysis, the mucin can be readily freed from bile salts, but not so readily from bile pigment; moreover, putrefaction is apt to ensue when dialysis is prolonged. The method ultimately adopted was to precipitate the mucin with five times its volume of absolute alcohol; the precipitate was collected and freed from alcohol by centrifugalising, redissolved in water, and again precipitated by alcohol. By thus repeatedly removing the alcohol, the mucin was not rendered insoluble. The properties of a 0·23 per cent. solution of this so-called mucin were as follows:—

On heating a neutral solution, it coagulated on boiling. After the addition of a trace of acetic acid, which caused no precipitation at the ordinary temperature, it coagulated on heating, like a proteid solution. More acetic acid caused precipitation without heat, and the precipitate dissolved in excess although with some difficulty; this acetic acid solution was precipitated by potassium ferrocyanide, potassio-mercuric iodide, mercuric chloride, and tannic acid. Hydrochloric acid in very small quantities caused a flocculent precipitate,

which dissolved easily in excess. Copper sulphate, ferric chloride, potassio-mercuric iodide, lead acetate, and potash alum gave abundant precipitates when added to a neutral solution. Saturation with sodium chloride or magnesium sulphate gave precipitates; the solution also gave the xanthoproteic, Millon's, and Adamkiewicz's reaction.

A solution of the mucin in hydrochloric acid (0.3 per cent.) gave no precipitate when digested for some time at 40°; but if pepsin were first added, a flocculent precipitate formed, as in solutions of nucleo-albumins. Prolonged heating with dilute mineral acids yielded no reducing substance.

The following are the results of elementary analysis:—C, 50.89; H, 6.735; N, 16.14; and S, 1.66 per cent.

The so-called mucin of bile is regarded, not as true mucin, nor as a mixture of globulin with bile salts, but as a nucleo-albumin. Small quantities of true mucin derived from the walls of the gall-bladder appear to be also present in certain cases.

W. D. H.

Physiological Chemistry.

Relation of Carbohydrates in Food to Digestive Ferments.

By A. STUTZER and A. ISBERT (*Zeit. physiol. Chem.*, **12**, 72—94).—The question of the artificial digestion of carbohydrates is taken up from the same point of view as that of proteids (Abstr., 1887, 361, 388, 1229); namely, can quantitative estimations be obtained of the digestible and indigestible portions of carbohydrates by the successive treatment of the fodder with the various diastatic ferments? It is already well known that certain carbohydrates, such as starch and sugar, are more digestible than certain others, such as cellulose, which is not attacked by the digestive juices, but only by putrefactive agents.

Standard solutions of ptyalin (from pig's salivary glands) of malt diastase, of pepsin, and of pancreatin were prepared; the two last being the same as those used in previous experiments. Ptyalin acts best at 40°, diastase at 60°; pancreatic fluid acts on starch better in a neutral than an alkaline fluid: not at all in an acid one. Clover-hay, wheat-meal, and white bread were the kinds of food used; and tables are given of the proteid, fat, carbohydrate, ash, and water in each of these. Fat was in all cases first removed by extracting with ether. 2 grams of the food was used in each experiment; this was boiled with 100 c.c. of water, and when cool the ferment solution was added; 200 c.c. of the ptyalin solution with which it was kept at 37—40° for two hours: or 25 c.c. of the solution of diastase for the same length of time at 60—65°. The residue was then filtered off through asbestos, and exposed to the action of 400 c.c. of the peptic fluid; it was again freed from digestive fluids by filtration before being exposed for three hours to the action of the pancreatic

ferment at 37—40°. The weight of the final residue (*minus* ash, the carbonic anhydride being driven off by nitric acid) gave the undigested organic substance (*a*); the nitrogen in this was estimated, multiplied by 6.25, and the product gives the undigested proteid (*b*); the difference between (*a*) and (*b*) gives the undigested carbohydrate.

The *first* series of analyses are those in which the food was subjected either to the action of ptyalin or diastase, and to the subsequent action in most cases of pepsin. Full details in tabular form are given of these and the following analyses; and the following conclusions are drawn:—

(1.) A feebly alkaline solution of ptyalin acts better than a neutral, and this better again than a feebly acid one.

(2.) For substances which are rich in digestible carbohydrates, like wheat-meal, the optimum of digestion with a neutral ptyalin solution (which was the one usually employed) was obtained when 100 c.c. of the solution was present to every gram of the food. When food, such as hay, in which the digestible carbohydrates was small in quantity was used, half this amount sufficed.

(3.) 25 c.c. of the diastase solution was sufficient.

(4.) Ptyalin alone worked better than diastase, but when followed by the action of pepsin they gave identical results.

(5.) Neutral ptyalin solution dissolves some amount of proteid.

The *second* series of analyses was one in which the pancreatic fluid alone acted. 100 c.c. of the neutral fluid gave the optimum of digestion on the carbohydrates, but the action was not so great as with ptyalin or diastase alone. Alkaline pancreatic fluid acts best on proteids.

The *third* series were experiments in which the action of ptyalin or diastase was followed by that of the neutral pancreatic fluid: the best results being obtained when ptyalin was first used. The additional action of the pancreas is, however, very small.

The *fourth* series were experiments in which the action of either ptyalin or diastase was followed by that of both pepsin and pancreatic ferment; but the optimum was the same whether ptyalin or diastase was used. Although the pancreatic juice by itself acts on amyloids best when neutral, yet, after the action of the other ferments, the best results are obtained when it is feebly alkaline.

It is not, however, believed that these results are comparable with what is obtained in natural digestion, because the bacteria which occur in the intestines and which act so energetically on carbohydrates, are left out of account. It is possible, however, that the method of artificial digestion may furnish us with a means of estimating cellulose quantitatively.

W. D. H.

Changes in Carbohydrates in the Alimentary Canal. By J. SREGEN (*Pflüger's Archiv*, 40, 38—48).—Cane-sugar and starch are the carbohydrates most used as food; the former is inverted in the stomach (Hoppe-Seyler); the latter is converted into erythrodextrin in the stomach, and sugar is formed from it in the intestine by the action of the pancreatic and, according to some, of the intestinal juice also. Nasse named the sugar so formed ptyalose; v. Mering and

Musculus showed that this is identical with maltose. On the other hand, the sugar present in the blood and that which leaves the liver is dextrose.

The present research is devoted to a reinvestigation of these points. Animals were fed for some days on cane-sugar, and then killed; the contents of stomach and intestines were examined, and the following conclusions drawn: the stomach inverts sugar; besides cane-sugar, a certain quantity of reducing sugar was also found. The small intestine contained no cane-sugar; after boiling the contents with hydrochloric acid, the amount of sugar remained the same; the sugar present is therefore invert sugar; 24 hours after death, no sugar is found in the stomach, and only traces in the intestine, the sugar having been changed into lactic acid. In the portal blood, a certain quantity of reducing sugar is found, but after boiling with acid there was no increase in reduction, showing that cane-sugar is not absorbed as such, or if it is, in such small quantities as not to be recognisable by this method; the latter is probably the more correct statement, as cane-sugar is sometimes found in the urine.

In experiments in which starch (starch-meal, potatoes, and rice) was used, it was found that erythro-dextrin was present in the stomach, but only traces of sugar which might have been formed by the saliva. The small intestine also contains dextrin, probably achroo-dextrin, and a reducing sugar; on boiling the contents of the small intestine with acid, the reducing power is increased; this is due to the conversion of dextrin into sugar; if the dextrin is first precipitated by alcohol, and the residue treated with acid, there is no increase in the reducing power; the sugar is therefore grape-sugar. It is possible that starch is converted into maltose by the pancreatic secretion, and then by the further action of the intestinal juice into dextrose (Brown and Heron, *Abstr.*, 1880, 903). Absorption takes place so rapidly that only small amounts of the products of digestion are obtainable. In the portal blood, dextrose was found, and in one instance dextrin also.

W. D. H.

From what Material does the Liver form Sugar? By J. SEEGEN (*Pflüger's Archiv*, **40**, 48—64).—The liver continues to form sugar after removal from the body; in fact, as long as its cells retain vitality and the quantity formed is not in proportion to the glycogen lost (Seegen and Kratschmer, *Abstr.*, 1882, 540). By researches of three kinds, (1) using various materials, for instance, peptones as food; (2) injecting these substances into the blood; and (3) placing the excised liver in contact with them, it was shown that peptone was one substance from which the liver forms sugar. The blood in the hepatic vein contains twice as much sugar as the portal vein, whether the food contains carbohydrate or not; fat and proteid seem to be the substances from which the liver normally forms sugar. The sugar formed from glycogen by diastatic ferments is maltose, whereas that found in the blood leaving the liver is dextrose.

Chittenden and Lambert (*Studies from Lab. Physiol. Chem.*, Yale Univ., 1885) obtained results which showed that although the total carbohydrates are increased by peptone, the sugar is increased but

little; they adhere to the view generally held that the sugar is formed from glycogen. They also speak of the sugar which leaves the liver as a mixture of maltose and dextrose. A large amount of the present paper is devoted to a criticism of the methods and results of Chittenden and Lambert.

W. D. H.

Fate of Lecithin in the Body. By K. HASEBROEK (*Zeit. physiol. Chem.*, **12**, 148—162).—Bokay (*Zeit. physiol. Chem.*, **1**, 157) showed that the pancreatic juice splits lecithin into a fatty (oleic, palmitic, or stearic) acid, choline or neurine, and glycerophosphoric acid. The question which is investigated in the present research was what happens to these three products of decomposition. The fatty acid doubtless behaves like fatty acids from adipose tissue, being partly saponified and separated from the body as calcium compounds, partly absorbed and further oxidised in the body to form carbonic anhydride and water. Choline, as has been shown by Brieger's work on ptomaines, is a type of poisonous alkaloids obtained by the putrefaction of organic substances. It is perhaps here also obtained from lecithin, which has a wide distribution in the animal kingdom. Putrefaction has an important part to play in the alimentary canal. The process of putrefaction in both neurine and glycerophosphoric acid outside the body was studied according to Hoppe-Seyler's method and with the apparatus used by him (*Zeit. physiol. Chem.*, **1**, 561). A mixture of choline hydrochloride, sewer-mud, calcium carbonate and water was kept at the ordinary temperature, and the gases which came off in large quantities were collected and analysed. They were found to consist of carbonic anhydride 18 to 20, and methane 80 to 82 per cent. After two months, when all evolution of gas had ceased, the liquid residue was examined microscopically, zoogloea colonies being found. Some was injected hypodermically in a rabbit but without ill results. On analysis it was found to contain large quantities of ammonia, and traces of first substitution products; of higher substitution basic products such as trimethylamine there was none. If a similar decomposition occurs in the intestine, it may be concluded that carbonic anhydride, methane, and ammonia are formed from choline there. This gives us a fresh source of methane in the intestine; Hoppe-Seyler and Tappenier (*Abstr.*, 1887, 1131) have shown that cellulose is one source; and Hoppe-Seyler (*Abstr.*, 1887, 1135) has shown that acetates form another. Choline, moreover, is not an unimportant source of marsh-gas, as lecithin is largely contained in eggs, meat, and in leguminous and other seeds.

On subjecting glycerophosphoric acid to similar treatment, it was not found to yield any gases, or only minute quantities such as probably came from the mud used. The conclusion is therefore drawn that the acid is absorbed as such. This coincides with the observation of Sotnischewsky (*Zeit. physiol. Chem.*, **4**, 215), who found it unaltered in the urine.

W. D. H.

Relative Nutritive Value of Fat and Carbohydrate. By O. KELLNER (*Zeit. physiol. Chem.*, **12**, 113—115).—By feeding a horse on starch and linseed oil respectively, and calculating the work done, it

was found that the energy of one part of fat is equal to that of 2.6 parts of starch.

W. D. H.

Feeding with Earth-nut and Palm Cake. By M. SCHRODT (*Bied. Centr.*, 1887, 624—626).—The animals employed were cows, and they were fed with palm-nut cake containing 15 per cent. albuminoids, whilst in the other periods of feeding they received earth-nut cake, which contained three times that quantity.

Earth-nut cake cannot be replaced by a similar quantity of palm cake without a loss of milk, fat, and dry matter; and cotton cake produces the best results of all known cakes.

E. W. P.

Change of Chemical Composition of Muscle by Fatigue. By A. MONARI (*Gazzetta*, 17, 367—385).—In this paper a further account is given of the variation of the chemical composition of muscle induced by fatigue. Full-grown dogs were killed after repose and after protracted exercise, and their muscles separated and worked up by well-known methods. The relation of creatine to creatinine was determined in each case and the results are set forth in extensive tables. The main conclusions arrived at are that (i) the proportion both of creatine and creatinine is increased by fatigue; (ii) in certain conditions of labour, the proportion of creatinine can exceed that of the creatine by one-half; (iii) in some cases the quantity of creatine in the wearied muscle is less than that present in the muscle in a state of repose, but then a greater proportion of creatine is formed owing to the transformation of the one into the other; (iv) that the creatinine is produced by transformation of the creatine; (v) xanthocreatinine is also produced, and in a proportion about one-tenth of the creatinine.

V. H. V.

Formation of Xanthocreatinine in the Organism. By A. MONARI (*Gazzetta*, 17, 360—362).—In this paper in addition to the previous observations (*Abstr.*, 1887, 615) an analysis is given of the compound of xanthocreatinine with zinc chloride, which points to a formula $(C_5H_{10}N_4O_2)_2, ZnCl_2$. This substance cannot however be completely separated from the similar compound with creatine.

V. H. V.

Scatoxylsulphuric Acid and Scatole Pigment. By B. MESTER (*Zeit. physiol. Chem.*, 12, 130—144).—Brieger (*Zeit. physiol. Chem.*, 4, 414) showed that scatole when administered to animals leaves the body in the urine as an ethereal hydrogen sulphate, and the chromogen of a red pigment is often also observed; this occurs also in human urine. J. Otto (*Pflüger's Archiv*, 33, 614) obtained this pigment from the urine of a diabetic patient in considerable quantity, and showed by its reactions and analysis that it consisted of scatoxyl potassium sulphate. In the present experiments, scatole was prepared synthetically by E. Fischer's method (*Abstr.*, 1886, 806), and it was given in doses of 6 grams daily to a dog; it was afterwards found advisable to reduce this to half, as so large a dose caused sickness occasionally but never diarrhoea. Observations were made on the relations of the normal sulphates and the ethereal hydrogen sulphates, but the variations were within normal limits. The

urine passed during three weeks was collected, and G. Hoppe-Seyler's method (*Zeit. physiol. Chem.*, 7, 423) for the separation of salts of indoxylsulphuric acid was adopted for the preparation of scatoxyl potassium sulphate, but unsuccessfully, either none of the salt or the merest traces being obtained. The pigment cannot therefore be a compound of scatoxylsulphuric acid, but the chromogen is of an unknown nature. The urine used contained abundance of the pigment, which was formed by adding hydrochloric acid to an alcoholic, ethereal, or watery extract of the evaporated urine. The urine also reduced alkaline copper hydroxide solutions, and was lævorotatory. A series of observations were made on the daily relations of ordinary sulphates to ethereal hydrogen sulphates, and the quantity of pigment present in the urine during the administration of scatole. Of 12 grains given during seven days, not more than one-fifth was passed as scatoxylsulphuric acid. There is a slight increase of ethereal hydrogen sulphates produced in the urine by giving scatole, and the normal sulphates are slightly diminished. After prolonged feeding on scatole, however, the ethereal hydrogen sulphates are diminished in the urine, this may be due to scatole being an antiseptic; moreover the quantity of pigment varies without any fixed relation to the amount of these compounds. The pigment is apparently an oxidation product of the chromogen, as its formation is prevented by the simultaneous action of reducing agents like nascent hydrogen.

Elementary analyses are not concordant, but the author considers that they approach to what would be attained from scatoxyl itself; he considers that the pigment is an oxidation product of scatoxyl with a simultaneous condensation of two molecules. It is amorphous; on heating it loses 10 per cent. of water. A solution of the chromogen at first colourless becomes dark-violet and later brown on exposure to air. It dissolves in hydrochloric and sulphuric acids with a red, and in alkalis with a yellow colour. It is soluble in alcohol, amyl alcohol, ether and chloroform, but not in water. It is apparently unaltered by ammoniacal fermentation.

A certain part of the scatole is found unchanged in the fæces. The result of giving scatole as food thus differs considerably from what follows the administration of indole. The property of the urine in rotating polarised light to the left may indicate that the chromogen is a compound of glycuronic acid analogous to indoxylglycuronic acid.

This pigment is perhaps the same as the pigment described in normal human urine under various names—urorubin, urosein, uroerythrin, purpurin, &c.

The effects of administering phenylhydrazinepyruvic acid to animals with their food shows that it is a powerful poison, producing blood in the urine among other symptoms.

W. D. H.

Animal Gum. By H. A. LANDWEHR (*Pflüger's Archiv*, 40, 21—37).—Animal gum (Abstr., 1887, 26) is present in greater abundance in foetal life than in extra-uterine life; it is present in the Whartonian jelly, it is in excess in the connective tissues, and the chondrogenous tissue (cartilage) which precedes the long bones appears to

consist of collagen combined with animal gum; the latter compound is replaced by calcareous salts in adult bone. In some animals, as the frog, the gum is derived from the mucinoid envelope of the eggs; in mammals, from the uterine glands, which are enormously developed during pregnancy. Pathological conditions of the female generative organs are often associated with excess of mucin or other compounds which yield gum; such as ovarian cysts, which contain metalbumin (pseudomucin): goitrous colloid cysts do not yield gum. Myo-œdema, a disease first described by Gull and Ord in women, is associated with increase of mucin in the cutaneous tissues (Charles, *Med.-Chirurg. Trans.*, 71, 57), and may, perhaps, be associated with disease of the genital organs. Chlorosis is a form of anæmia which seems limited to women at about the age of puberty. The administration of iron in this disease causes great increase in the hæmoglobin of the blood; Hamburger, among others, has shown, however, that little or no proportion of the medicinal preparations of iron is absorbed from the alimentary canal, but iron is absorbed only in the form of organic compounds, such as are formed in the processes of plant life. Moreover, the quantity of iron is only 3 grams in the whole body, and this quantity is taken many times over during treatment. Bunge explains (Abstr., 1885, 574) the usefulness of iron in this affection by its forming iron sulphide in the intestines, removing the excess of sulphur in this way from the body; in chlorosis due to excessive fermentation processes in the alimentary canal, large quantities of hydrogen sulphide are formed, which destroy the organic compounds of iron that form hæmoglobin (hæmatogen); the administration of iron prevents this destruction of the hæmatogen. The limitation of chlorosis to the female sex, and to the time of puberty, leads the author to doubt this explanation. He regards the disease as one produced by excessive development at this period of the substances containing gum necessary for the nourishment of the embryo, and which acts injuriously on the hæmoglobin molecule; iron precipitates the gum in the alimentary canal as a jelly-like coagulum (as it does vegetable gum), and thus excess of gum leaves the body with the fæces.

The hypothesis formerly advanced as to the function of the gum in the stomach requires to be modified as follows:—In the lumen of the gastric glands which is filled with mucus, a ferment is produced by stimulation, which forms lactic acid from the gum of the mucus, and this by acting on sodium chloride produces free hydrochloric acid and sodium lactate; the former is poured into the stomach, the latter is absorbed from the glands. During digestion, the amount of sarcolactic acid in the blood is increased from 0.02 to 0.1 per cent. (Drechsel). In phosphorus poisoning, this acid is found in the urine, and also excess in the gastric juice (Cahn, Abstr., 1886, 1053); the intestinal mucus in these cases remains neutral.

In the intestine, the function of animal gum seems to be to aid the emulsion, and also the absorption of fats; pancreatic juice is not necessary for this purpose; parotid saliva, which although it contains no mucin, contains free animal gum, will emulsify fats.

Thierfelden (*Pflüger's Archiv*, 32, 619) found that in the mammary

glands milk-sugar is formed by a fermentation process, at the body temperature from a mother-substance which is not glycogen. This substance is animal gum; a watery decoction of rabbit's milk-glands was freed from proteid by heat, from milk-sugar by two days' dialysis; it was then evaporated to a small bulk, saturated with sodium sulphate, and filtered. The filtrate contained animal gum, and gave the characteristic blue flocculi with copper hydroxide. Probably in the same way that starch is hydrated to form sugar in the intestines, and in the liver again dehydrated to form glycogen, so milk-sugar undergoes similar changes, which after being inverted into galactose in the alimentary canal is absorbed, and then dehydrated in the body, and stored as animal gum. If this is so, chlorotic people should take no carbohydrate food. In flesh feeders, it is probable that gum, like glycogen, is formed from proteid.

Quantitative investigations on animal gum are at present impossible. The conversion of the gum, $C_6H_{10}O_5$, into gummose, $C_6H_{12}O_6$, a reducing substance, is slow and incomplete. It is, moreover, precipitated at least partially by the precipitants of proteids, neutral salts, alcohol, copper sulphate, ferric chloride, &c. W. D. H.

[*Note by Abstractor.*—Myxœdema has been since found to be present in men nearly as often as in women; no constant relation has been found to exist between disease of the generative organs and myxœdema; moreover, subsequent analyses have not confirmed Charles's statement as to the high percentage of mucin in the cutaneous tissues.]

Animal Dextran. By L. LIEBERMANN (*Pflüger's Archiv*, **40**, 454—459).—*The Schizoneura lanuginosa* is a gall-producing louse which attacks elms. In the interior of the gall are found masses of a secretion from the animal's body which are at first clear drops, but when the galls dry up in the autumn, it consists of dirty-brown, irregular masses. The properties of this substance were investigated as follows:—The masses were finely divided, and boiled with distilled water; the resulting greenish-brown cloudy solution was decolorised to a great extent by animal charcoal, and filtered; it was acidified with hydrochloric acid, and precipitated with 96 per cent. alcohol. The precipitate was washed with alcohol, dried over sulphuric acid, and analysed; the substance contained no nitrogen, and the percentage composition corresponds very closely with the formula $C_6H_{10}O_5$. Its specific rotation is $[\alpha]_D = +156.7$. This substance has the physical appearance of gum, is soluble with difficulty in cold, more easily in boiling water; it is insoluble in alcohol and ether, and neutral in reaction. On burning it, it gives out a smell like that of burning paper. It does not reduce copper or bismuth salts. With potash and copper sulphate, a greenish-blue, jelly-like coagulum is formed soluble in hydrochloric acid; from this acid solution, the gum is precipitated by alcohol. In the watery solution, lead acetate gives no precipitate, if alcohol is present, however, as well, it gives a precipitate; iodine gives no colour; picric acid and potash also give no reaction. On heating for a long time with dilute sulphuric acid, a

substance which reduces copper oxide is formed; it differs from all known gums by its high rotatory power; it seems not to be identical with Landwehr's animal gum, and the name animal dextran (compare Scheibler, *Wagner's Jahrsber.*, 1875, 790) is suggested for it.

W. D. H.

Nephridia and Liver of *Patella Vulgata*. By A. B. GRIFFITHS (*Proc. Roy. Soc.*, **42**, 392—394).—The nephridia were dissected from the bodies of a large number of fresh limpets, and the secretions of the left nephridia examined separately from those of the right nephridia. Chemically, the secretions on the two sides were found to be identical; the clear liquid was first treated with hot dilute sodium hydroxide, and then hydrochloric acid added, and rhombic crystals obtained, which gave the murexide test; crystals of uric acid were obtained by evaporating the secretion to dryness; the residue was taken up with absolute alcohol, filtered, dissolved in hot water; on adding excess of acetic acid to this, and allowing the mixture to stand seven hours, crystals of uric acid were obtained. The liver of patella was found to possess the functions of a true pancreas, like the "Cephalopod liver." The secretion converts starch into glucose, it produces an emulsion with fats, and a soluble ferment extracted from the cells of the gland converts fibrin into leucine and tyrosine. The secretion contains proteids, leucine, and tyrosine, but no biliary acids. Glycogen also could not be detected in either the organ or its secretion.

W. D. H.

Absence of Uric Acid and Alkaline Reaction in the Urine of Carnivoræ. By G. SANARELLI (*Chem. Centr.*, 1887, 804—805; from *Ann. Chim. Farm.*, 1887, 273—285).—The reaction of urine from two young foxes was found to be strongly alkaline, both after a flesh and after a mixed diet; uric acid was absent and hippuric acid initially present was replaced by benzoic acid. Ammoniacal fermentation quickly set in, although the urine did not contain an abnormally large quantity of bacteria even for acid urine. Albumin, sugar and hæmatin were absent. With a flesh diet, the alkalinity increased, but with a bread diet it decreased and changed suddenly into an acid reaction, although both uric and hippuric acids were absent. The alkalinity was ascertained by means of litmus and not by phenolphthaleïn.

V. H. V.

Presence of Hydrogen Sulphide in Urine. By F. MÜLLER (*Chem. Centr.*, 1887, 807; from *Berl. klin. Wochenschr.*, **24**, 405—408 and 436—437).—The formation of hydrogen sulphide in urine from fermentation (hydrothionuria) is doubtless conditioned by micro-organisms. It is here shown that its formation is due neither to albumin nor cystin, nor potassium thiocyanate, nor yet to the presence of sulphates. On adding a solution of hydrogen sulphide to normal urine, it is quickly oxidised into water and sulphur, even in absence of air, thus showing that in cases of hydrothionuria the urine must have lost this oxidising property. On the other hand, if hydrogen sulphide is added to urine from which the hydrogen sulphide reaction originally present has disappeared, its presence could be detected for a considerable time; this proves that the bacteria con-

sumed all the available oxygen, and thus the oxidation of the hydrogen sulphide could not ensue. V. H. V.

Ethereal Hydrogen Sulphates in Morbid Urines. By G. HOPPE-SEYLER (*Zeit. physiol. Chem.*, 12, 1—32).—Tables are given of the amounts of sulphuric acid combined as sulphates (*a*) and that combined as ethereal hydrogen sulphates; (*b*) and the ratio *a* : *b* in the urine of patients suffering from a variety of diseases. The details of the chief cases are also given. The general results obtained may, however, be summarised as follows:—Deficient or increased absorption of the normal products of digestion, as in peritonitis, tubercular diseases of the intestine, &c., leads to an increase of ethereal hydrogen sulphates in the urine, as the normal products of digestion undergo putrefactive changes, and these putrefactive products are absorbed from the intestine. In typhoid fever, there is no such increase. Simple constipation also causes no change. Diseases of the stomach in which the food lies in the stomach a long time and then undergoes fermentative changes, always lead to increase of the ethereal hydrogen sulphates. Putrefactive changes outside the alimentary canal, putrid cystitis, putrid abscesses, peritonitis putrida, &c., have the same result; and the result is proportional to the severity of the putrefaction, increased by the retention and diminished by the discharge of putrid matter as, for instance, on opening the abscess. The quantity of the ethereal hydrogen sulphates may, however, be unaltered, if at the same time other products of putrefaction are increased. Such a relation is seen between indoxyl and scatoxyl. In normal human urine, scatoxyl predominates over indoxyl; in peritonitis, the reverse the case. W. D. H.

Determination of Urea and Total Nitrogen excreted hourly in Urine. By E. GLEY and C. RICHET (*Compt. rend. Soc. Biol.* [8], 4, 377—385).—Hourly determinations of the quantity of urine and the percentage of urea, extractives and total nitrogen contained therein have been made by the authors for four consecutive days. The following are the conclusions:—

1. The greatest elimination of water takes place about one hour after a meal; the greatest elimination of urea three to four hours after.
2. The excretion of water and nitrogen is much less during the night than during the day.
3. With the same diet, two persons of different body-weight excrete almost the same amount of nitrogen.
4. The ratio between the excretion of urea, extractives and total nitrogen remains almost constant throughout the 24 hours.
5. The ratio of nitrogen as urea to total nitrogen is about 4 to 5.

J. P. L.

A New Pathological Colouring Matter from Urine. By W. LEUBE (*Zeit. anal. Chem.*, 26, 672).—The urine in a case of osteomalacia turned black in the air. Ether took up the colouring matter with red-violet colour, and on evaporation left it as a resinous mass, soluble for the most part in water, and wholly in ether, benzene,

chloroform, and alcohol. Alkalis removed the colouring matter from its ethereal solution, becoming first brown-red and then yellow. Strong hydrochloric acid dissolved the colouring matter unchanged; the colour disappeared on heating. Zinc-dust decolorised the solution; the colour returned on exposure to air. No characteristic absorption-spectrum could be seen.

M. J. S.

Urinary Pigments. By L. v. UDRÁNSZKY (*Zeit. physiol. Chem.*, **12**, 33—63).—In continuation of this research (see Abstr., 1887, 1135), the first question investigated was what constituent or constituents of normal urine yield these products. Hoppe-Seyler states that humous substances, when heated with potash, yield pyrocatechuic acid, volatile fatty acids, and a non-nitrogenous acid, which are the same products as those derived from the pigment. It was found that the non-nitrogenous residue from the humous substances prepared from normal urine, from diabetic urine, or from a mixture of urea and dextrose, has the same composition. The conclusion is drawn that the dark colour which occurs in urine on treating it with mineral acids is due to a formation of such substances. They are formed by the decomposition of the reducing substance of normal urine, and their quantity stands in a constant relation to the reducing power of the urine. By boiling the urine for at least 18 hours with hydrochloric acid, the complete separation of the humous substances is brought about, and the urine loses its reducing power. The indoxyl compounds in the urine have probably only a very small influence in the formation of these substances. Humous substances containing nitrogen can be formed from carbohydrates in the presence of nascent ammonia. As Thudichum first remarked, there can no longer be any doubt that Proust's fallow resin, Scharling's omichmyl oxide, Heller's nrrrhodine, Schunck's indirubin, Scherer's pigment from urine, Harley's urohæmatin, and Marcet's immediate principle, are different expressions for one and the same mixture of substances, namely, of some of the products of decomposition by acids or ferments, under the influence of air or heat of the normal yellow pigment of the urine. The uropithin, uromelamin, and omicholic acid of Thudichum, Heller's nrophæin, and several others can now be put into the same category; it is also possible to go a step further and say that the mother-substance of these artificially prepared pigments is the reducing substance of urine, and the normal yellow colour of urine is due to the change of carbohydrates into humous substances which has commenced inside the body.

The dark colour of the urine of herbivora (horses) depends on the presence of some constituent of the hay; the colour itself is due to a humous substance formed from this material in the fodder.

The dark colour of the urine after the administration of carbolic acid (carboloria) is also due to a similar substance. W. D. H.

Ferments in Human Fæces and in the Contents of Cysts. By R. v. JAKSCH (*Zeit. physiol. Chem.*, **12**, 116—129).—The contents of abdominal cysts and ascitic fluid have a diastatic action; the blood and other tissues and fluids of the body have also been described as

having a similar action. The presence of such a ferment in the contents of pancreatic cysts cannot therefore be considered diagnostic.

The fæces of children were examined for a similar ferment, and in 30 cases of various diseases, it was found that the fæces themselves, as well as a glycerol extract of them, had a marked diastatic action on starch in most cases. Sugar was tested for by Trommer's, Nylander's, Rubner's, and the phenylhydrazine tests, and abundance was found in 25 cases. In three cases only a small amount of sugar was formed; these were cases of pneumonia, rickets, and acute nephritis respectively; in two cases only (chronic intestinal catarrh and general atrophy respectively) did the ferment appear to be absent. Whether this ferment is derived from the pancreas, or is due to the action of micro-organisms, or is the result of the presence of certain proteids (Seegen and Kratschmer having shown that egg-albumin, serum-albumin, and casein have an amylolytic action, *Pflüger's Archiv*, **14**, 593), is uncertain. Possibly all these factors come into account. A second series of experiments similarly conducted proved the presence of a ferment, which, with one exception, was soluble in glycerol, and which had the power of inverting cane-sugar. This ferment may be derived from the intestinal juice (O. Loew, *Pflüger's Archiv*, **27**, 203; Pavy, *Maly's Jahresber.*, **14**, 294). The action is certainly not due to the action of acids in the fæces, as it is present in alkaline fæces also.

Both these ferments are present in healthy fæces, and in adults as well as in children. Their absence in cases of disease may be found to be of diagnostic value; but this question, as well as that of the influence of these ferments on food introduced per rectum, must be left until more is known about them. The presence of ferments shows probably that some action more important than the mere absorption of water goes on in the large intestine.

W. D. H.

Hæmoglobin Crystals in Septic Diseases. By C. J. BOND (*Lancet*, **2**, 1887, 509—511, 557—560).—If normal human blood is drawn from the finger, placed on a slide, and covered with a cover-glass, no crystallisation of the hæmoglobin occurs. If, however, a drop of putrid serum is added, crystallisation occurs in 24 to 48 hours. The blood drawn from the finger of patients suffering from septic poisoning has the same tendency to crystallise without the addition of any serum. In pyæmia, the effect is not so marked; in the blood from the red patches of erysipelas there is the same tendency for crystallisation to occur after removal from the body, whereas this does not occur in blood drawn from other parts of the body; in cancrum oris, which is an emphatically infective process, the same phenomenon is observed; whereas in the common zymotic diseases the blood behaves normally. The presence of sugar in the blood in diabetes, or the nitrogenous substances in uræmia, or the supposed lactic acid in rheumatism, or the bile salts in jaundice, is also not sufficient in itself to cause the crystalline tendency. In Addison's disease and in leucocythæmia, the crystalline tendency is well marked, whereas in ordinary anæmia, and often in pernicious anæmia, it is absent. In leucocythæmia the change is evidently connected with the presence of excess of white

corpuscles, or some product of their decomposition; cancer cells, and the cells of other rapidly growing tumours, act similarly to leucocytes in this particular. It is found that in 10 or 12 hours after death in persons who have died from accident, the crystalline tendency is present in the blood removed from the heart, and absent in that removed from the limbs; this is probably because the blood in the heart is within easy reach of the septic gases formed in the intestines.

The larger domestic animals resemble man in the matter of crystallisation of hæmoglobin; but in the seemingly healthy mouse crystallisation occurs readily in the unaltered blood; in the cat there is a similar but not so well marked a tendency, especially in blood drawn from the splenic vein.

The occurrence of this tendency in man under the conditions described above, especially in septic diseases, is supposed to be due to the formation or presence of some ferment produced, either by the growth of bacterial organisms, or as in leucocythæmia, by the disintegration of animal cells; the stages in the change which this ferment works being first a deoxidising action on the hæmoglobin, then its exudation into the serum, and lastly crystallisation.

W. D. H.

Physiological and Therapeutical Action of Hyoschine Hydrochloride. By E. GLEY and P. RONDEAU (*Compt. rend. Soc. Biol.* [8], 4, 56—57, and 163—164).—Hyoschine hydrochloride and hydrobromide are rapid, powerful, and unirritating mydriatics, acting more rapidly and for a more prolonged period than atropine. One drop of a 1 per cent. solution produces the maximum dilatation and paralysis of accommodation in 8 to 10 minutes.

In the rabbit and dog, the pupil of the other eye is affected, dilatation and temporary paralysis of accommodation occurring. This is not the case in man, so far as the authors' observations go.

If the cervical sympathetic of a rabbit is severed on the same side as the eye treated with the mydriatic, further dilatation of the pupil takes place on stimulating the proximal end of the nerve. The hydrochloride exercises the same effect as atropine on the inhibitory nerves of the heart, and diminishes or even suppresses the secretion of saliva, excitation of the chorda tympani with even strong currents being without effect on the submaxillary gland.

Both the hydrochloride and the hydrobromide act as powerful sedatives.

J. P. L.

Sodium Benzenesulphinate as an Antiseptic for Wounds. By E. HECKEL (*Compt. rend.*, 105, 896—898).—This compound is readily obtained by dissolving benzoic acid in a concentrated solution of sodium sulphite. It is very soluble in water at the ordinary temperature, and has no injurious effects even in somewhat large doses. It may be applied in the form of a solution containing from 4 to 5 grams per litre. It is more efficient than phenol, and ranks with mercuric salts and iodoform, without having the poisonous properties of the former or the disagreeable smell of the latter.

C. H. B.

Naphthol as an Antiseptic Medicine. By C. BOUCHARD (*Compt. rend.*, 105, 702—707).— β -Naphthol has already been used for external application, but has not been administered internally on account of its supposed high toxic power. From its comparative insolubility, however, it is a valuable antiseptic for deep wounds and for internal administration; 1000 c.c. of water dissolve 0.2 gram; 1000 c.c. of water containing 0.1 per cent. alcohol dissolve 0.33 gram; 1000 c.c. containing 5 per cent. alcohol dissolve 1.0 gram; 1000 c.c. containing 20 per cent. alcohol dissolve 2.0 grams. 0.33 gram of β -naphthol in 1000 c.c. of the usual cultivation liquids prevents the development of 11 species of bacteria, including those of anthrax, chicken cholera, and pneumonia, and a weak cultivation of the typhoid bacillus: it also retards the development of the bacillus of tuberculosis. It prevents the fermentation of urine, and the production of putrefaction by fæcal matter. Putrefying organic substances mixed with β -naphthol in the proportion of 0.2 gram per litre cease to putrefy, and soon lose their fœtidity.

In order to compare β -naphthol with other antiseptics, the author determined the quantity required to prevent the development of the bacillus which produces pyocyanine. 0.4 gram of β -naphthol per litre was required, and mercuric iodide was found to have six times the antiseptic power, phenol only one-sixth, creosote one-fourth. Mercuric iodide is, however, a violent poison, whilst β -naphthol may be introduced into the stomach of a rabbit in quantities not exceeding 3.8 grams per kilo. without producing death. Mercuric iodide has 250 times the toxic power. The fatal dose for a man of 65 kilos. would therefore be more than 250 grams, and it is only slightly more poisonous when injected subcutaneously. The poisonous action of β -naphthol is not observed with doses not exceeding 1.1 gram per kilo. per diem; the injurious effects previously observed must have been largely due to the mode of administration. The following table shows the comparative efficiency of the less poisonous insoluble antiseptics:—

	Antiseptic.	Doses per kilo.	
		Toxic.	Daily toxic.
Iodoform	1.27	0.50	0.05
Iodol	2.75	2.17	1.24
Naphthalene	1.51	3.40	1.00
β -Naphthol	0.40	3.80	1.10

C. H. B.

Localisation of Barium in the Organism after Chronic Poisoning with a Barium Salt. By G. LINOSSIER (*Compt. rend. Soc. Biol.* [8], 4, 122—123).—Neumann has recently shown in the case of rabbits, that after repeated injections of the insoluble sulphate into the veins, barium is to be found in the liver, kidneys, spleen, and spinal cord, but not in the muscles, thymus, and brain.

As the insolubility of the sulphate precludes the question of chronic poisoning, the author has made a similar series of experiments with barium carbonate, prolonging the chronic poisoning for a period of 30 days. He finds on analysis that all organs contain some barium,

but that it is present in very variable proportions. Lungs, muscles, and particularly the heart yield only traces, liver rather more, kidneys, brain, and spinal cord still more, and lastly bones a considerable quantity, as much as 0.56 in 1000 parts of bone ash. J. P. L.

Action of Acetanilide and Dihydroxynaphthalene on Blood.

By R. LÉPINE (*Compt. rend. Soc. Biol.* [8], **4**, 517—519).—Both acetanilide and dihydroxynaphthalene when administered as drugs produce after continued use a marked anæmic condition of the patient. The number of red corpuscles rapidly diminishes, and methæmoglobin is produced. J. P. L.

Saffron Substitutes. By T. WEYL (*Ber.*, **20**, 2835—2836).—

Commercial dinitrocresol is employed as a yellow colouring matter for butter, margarine, vermicelli, and confectionery. The author finds that it is poisonous, and that when introduced in aqueous solution into the stomach of rabbits in doses of 0.25 gram per kilo. it causes convulsions, paralysis of the pupil, and great difficulty in breathing, death ensuing from suffocation in from 20 to 30 minutes. Martius-yellow and the "butter-yellow" prepared by Griess from dimethylaniline and diazotised aniline are not poisonous. W. P. W.

Chemistry of Vegetable Physiology and Agriculture.

Studies on Pure Yeast. By C. AMTHOR (*Zeit. physiol. Chem.*, 12, 64—71).—The paper consists of comparative observations on the fermentative activity on wort of eight different kinds of yeast obtained from various German breweries. Observations were made on the amount of alcohol, extractives, specific gravity, glycerol, nitrogen, and reducing substances (reckoned as maltose). The colour intensity was also observed by Stammer's colorimeter.

The wort contained 10·8 of maltose; after fermentation, the sum total of sugar (that reckoned as alcohol + the maltose in the beer) was 11·34. In reality the increase was greater, as dextrin and maltodextrin are reckoned in the above as maltose. The increase is doubtless due to the conversion of dextrin into maltose. W. D. H.

Influence of the Age of Yeast on Alcoholic Fermentation. By P. REGNARD (*Compt. rend. Soc. Biol.* [8], 4, 442—444).—The influence on alcoholic fermentation exercised by the protoplasmic metamorphosis which occurs in the yeast cell when it is maintained under circumstances of complete starvation is represented graphically by the method introduced by the author in 1882.

The characteristic fermentation which yeast normally produces is lost after three days' complete starvation at a temperature of 25° to 30° J. P. L.

The Development of Free Nitrogen in Putrefaction and Nitrification. By O. KELLNER and T. YOSHII (*Zeit. physiol. Chem.*, 12, 95—112).—In the first experiments, beans, milk, and fish meal were allowed to putrefy, 20 to 50 grams of each being mixed with 10 c.c. of putrid urine and 33 c.c. of water, a small quantity of gypsum being also added. The quantity of nitrogen present before and after putrefaction was practically the same; no formation of nitrates took place. In a second series of experiments with (*a*) asparagine and (*b*) beans, earth was added, and also small quantities of monocalcium phosphate, precipitated tricalcium phosphate, and magnesium sulphate, for the favourable development of organised ferments (Warrington, *Trans.*, 1884, 637); no nitrification occurred, however, even after five months, and nitrogen estimations gave the same results as in the first experiments. There is thus no loss of nitrogen during putrefaction. Dietzell in experiments similar to those of Ehrenberg (*Abstr.*, 1887, 746) in the presence of oxygen, obtained different results. In the experiments made by the latter the putrefaction lasted six weeks, and there was no free nitrogen formed, whilst in those of the former, in which the experiments lasted 12 months, there was a loss of 15 per cent. of the nitrogen, that is to say, although putrefaction pure and simple does not cause the disengagement of gaseous nitrogen, certain processes of a secondary nature may perhaps do so. It may be due to the oxidation of ammonia by atmospheric oxygen. This could, however, not take place if organic substances are present which have a stronger affinity for oxygen; or it may be due to similar oxidation brought about by the action of nitrifying organisms, or by the action of free nitric acid on nitrogenous organic compounds; or it may be due to the reduction of nitrates and nitrites by organic substances, or, lastly, to a spontaneous decomposition of ammonium nitrate in dilute solutions.

In a third series of experiments, in which the earth used contained the nitrifying ferment, it was found that a loss of 9 to 10 per cent. of nitrogen accompanied the nitrification process; in which out of the possible ways enumerated above this takes place no definite statement can be made. Diluted sterilised solutions of ammonium nitrate do not appear to decompose spontaneously, but most probably the loss of nitrogen is due to a reaction between nitrites and organic nitrogenous compounds. When nitrification begins, the reaction of the urine, at first acid, becomes alkaline, and later neutral; this then remains unaltered. It appears possible that it is in the deeper layers of the mixture, or where the earth is specially rich in humus, that a portion of the nitrates or nitrites is reduced.

W. D. H.

Formation of Nitrogen during Putrefaction. By A. EHRENBURG (*Zeit. physiol. Chem.*, 12, 145—147).—A few further experiments illustrating the formation of methane and carbonic anhydride in putrefaction are detailed (*Abstr.*, 1887, 746).

W. D. H.

Dependence of Assimilation of Green Cells on their Respiration of Oxygen; the part of the Plant in which Oxygen

formed in Assimilation is produced. By N. PRINGSHEIM (*Ber. Akad. Ber.*, 1887, 763—777; compare *Abstr.*, 1886, 642).—The end cells of the leaves of *Chara fragilis* were enclosed in a microscopic gas-chamber, through which a mixture of hydrogen and carbonic anhydride (containing 1 to 5 per cent. of the latter) was passed. When light is excluded, the rotation gradually becomes less and less until at last (in 2 to 10 hours) the plasma is quite still. The cells, if not kept too long in this state, otherwise retain their original appearance, the chlorophyll apparatus remaining normal. On admitting oxygen, the rotation of the plasma again commences, unless the cells have been kept too long without oxygen after the protoplasm has ceased to rotate. If the cells are kept without oxygen just so long that the plasma still shows a slight movement, they will be found to have lost the power of assimilating, and when exposed to light, will no longer give off oxygen.

When the cells of *Chara* are exposed to light in a stream of hydrogen and carbonic anhydride, rotation of the plasma and evolution of oxygen cease after some time; in most cases the evolution of oxygen ceases before the rotation. The presence of the smallest amount of oxygen is sufficient (even after the rotation of the plasma has ceased for some time) to bring about movement and assimilation.

These results make it probable that in the decomposition of carbonic anhydride in plants no oxygen is formed, but that a compound is produced which decomposes at the outermost surface of the cells with evolution of oxygen.

The decomposition of carbonic anhydride and the evolution of oxygen do not occur together, but are distinct processes both as to time and place. Green and other tissues and plants in dying give off oxygen in the dark; the evolution of oxygen often continues for hours after the plant has died.

N. H. M.

Assimilation and Respiration of Plants. By U. KREUSLER (*Bied. Centr.*, 1887, 669—681).—In this continuation of former experiments (*Bied. Centr.*, 1887, 110) are given the details of experiments made with shoots of the same kind of plant, *Philadelphus grandiflorus*, at different stages of growth, the temperature of observation being 15° and 25°. At a temperature of 25°, a strong and marked decrease in assimilative power accompanies increasing age of the leaf; at 15° a maximum of assimilative power is noticed in the youngest leaves. This power reaches its minimum at the period of blossom, and again rises in the oldest leaves; so that between the assimilative power in the youngest and in the oldest leaves, there does not exist much difference. A table showing the amount of water absorbed at the different temperatures is also given. In the second portion of this paper, amongst many statements concerning the absorption and exhalation of carbonic anhydride at different temperatures, it is recorded that the range of temperature in which exhalation occurs is from 0—50°, and that it is greatest at the highest temperature, the maximum appearing to be at 46.4°. Assimilation seems to take place at a lower temperature than exhalation, and it is active at 50°; but the curve representing the relation of assimilation to temperature does not

agree with that representing exhalation at various temperatures. In the case of the bramble, the maximum intensity of exhalation occurs at about 46·6°, whilst that of assimilation is found at 25°. For further statements and arguments, reference must be made to the original.

E. W. P.

Physiological Signification of Tannin in Vegetable Tissues.

By M. WESTERMAIER (*Ber. Akad. Ber.*, 1887, 127—143).—The amount of tannin in living cells free from and containing chlorophyll increases with the amount of light to which the cells are exposed. Experiments made with *Quercus pedunculata* showed that the tannin migrates from the leaves downwards through the bark and the pith. It is uncertain whether starch and tannin migrate side by side without changing, or whether the starch migrates in the form of tannin.

In examining the leaves of *Rumex patens* and *Rheum raphaniticum*, a substance was found which showed the starch reaction with iodine and the tannin reaction with ferric chloride and with potassium dichromate. The colour produced in the starch reaction is a bright-blue, sometimes greenish, and sometimes deep sky-blue. The substance was found in large amount in the autumn leaves of *Rheum raphaniticum*.

N. H. M.

The Hop and its Constituents. By HAYDUCK (*Bied. Centr.*, 1887, 694—698).—Hops have no influence on alcoholic fermentation, but they retard, even if they do not wholly prevent, lactic fermentation, and this applies also to the butyric and other forms of like change, excepting the acetous, which is unaffected. Lerner and Bungener have shown that there exists in hops a white, crystalline compound, which they termed “hop-bitter acid.” This acid, on oxidation, forms a soft resinous matter, slightly soluble in water; besides the acid, a hard resin seems to exist in large quantities, and the authors have now discovered a third, soft resin. The method whereby it may be obtained is as follows:—The hops are first exhausted with ether, and after evaporation of the ether, the residue is treated with alcohol, which leaves a white wax undissolved; solution of lead acetate is then added to the alcoholic solution, when a yellow precipitate is produced, consisting of the soft resin in combination with lead. In the filtrate from this precipitate, the two other resins are found, the one soft and soluble in light petroleum, the other hard, insoluble in light petroleum, but soluble in alcohol and ether; the former is identical with that which is an oxidation-product of hop-bitter acid. All three seem to be feeble acids, and have no definite solubility in water, but the solution of the soft resins are intensely and disagreeably bitter; whilst that of the hard resin is slightly and agreeably bitter. As regards the suppression of lactic fermentation, although the hard resin has no effect, this property belongs to the soft resins. A resinous coating sometimes forms in the wort in brewing, and it has been generally ascribed to resin, but this view is now shown to be incorrect, as this coating contains only 4·6 per cent. of resin soluble in ether, whilst nitrogenous matter was present to the extent of 13 per cent. of nitrogen.

E. W. P.

Compounds extracted from *Anagyris Foetida*. By N. REALI (*Gazzetta*, 17, 325—329).—The seeds of the *Anagyris foetida*, on extraction with ether, yield a fatty oil, two resinous substances, and also a citron-yellow compound not further examined but probably a glucoside. From an alcoholic extract, glucose, saccharose, and a yellow substance are obtained, together with a compound having all the characteristics of an alkaloid, and called *Anagyrene*.

One of the above resinous substances which the author calls *anagyric acid* forms a lead salt, by means of which the acid can be isolated. It contains carbon, hydrogen and oxygen, but the analyses given are not very concordant. The oil is not desiccative, sp. gr. = 0.924 at 17°; on treatment with sulphuric and nitric acid, it acquires a blood-red colour. The oil yields a mixture of fatty acids on saponification. *Anagyrene* occurs as an amorphous mass of bitter taste, soluble in water, alcohol, ether, and benzene; it has an alkaline reaction and forms salts with acids. It gives all the reactions of alkaloids, such as precipitates with solutions of phosphomolybdic acid, potassium bismutho-iodide, and potassium mercurio-iodide. It is unaltered at ordinary temperature by sulphuric acid, but when warmed it evolves a musk-like odour. The platinochloride is an amorphous, yellow powder, the analysis of which pointed to a formula $C_{11}H_{34}NO_8$ for *anagyrene*.
V. H. V.

The Freezing of Ciders. By G. LECHARTIER (*Compt. rend.*, 105, 723—726).—The cider was cooled at -18° to -20° until nearly completely frozen, and the liquid portion was drawn off. The mother-liquor was denser and more highly coloured than the liquid obtained by melting the ice, which in the end yielded almost pure water. The mother-liquors were kept in a cellar for some months, and at the end of that time had a very fine colour and flavour. Addition of sugar to the must merely increases the proportion of alcohol, but concentration by freezing concentrates all the soluble substances from the apples. Concentration should not be carried beyond a certain point or a disagreeable flavour is developed, and for a similar reason only ciders of good original quality are suitable for this treatment. Even when the cider is kept at -18° for 12 hours, the ferment is not killed, although fermentation is retarded.
C. H. B.

Effects of an Electric Current on Wine. By F. MENGARINI (*Gazzetta*, 17, 441—450).—Blaserna and Carpène have previously made experiments on the effects produced on wine by the action of an electric current; these have shown that various oxidation products are formed, and the wine is artificially matured. In this paper, some further experiments on this subject are described, in which a current of 3.99 ampères per hour was passed for various periods of time through a sample of Italian wine; analyses were made of the wine without and with passage of the current and the results compared. The platinum electrodes were found to be covered with albuminous substances, blackened by oxidation; there was also a considerable deposit of these substances. The proportion of alcohol was diminished partly by the slight concomitant formation of acetic acid, partly also

by evaporation, and partly also by its destruction by a more profound oxidation. There was also imparted to the wine a perfume similar to that acquired by maturing; this increased by prolongation of the current. The passage of the current also assists its future preservation. The colouring matters are affected, but the author would not for the present draw any conclusions from his experiments. If by passage of an electric current the wine could be sterilised, so as to effect the complete removal of *Bacterium aceti*, this process would be of considerable technical importance. V. H. V.

Manuring Barley. By v. LIEBENBERG (*Bied. Centr.*, 1887, 649—651).—The experiments were conducted at 12 stations, and the manures employed were (1) Chili saltpetre, (2) Chili saltpetre and soluble phosphate, and (3) Chili saltpetre, soluble phosphate and potassium sulphate. The spring of the year (1886) was dry, whilst June and July were wet. There were three failures; of the remaining nine stations, the nitrogen showed itself active in producing corn and straw at seven stations, whilst an influence on the straw only was manifested at two. In two cases, potash increased the corn and straw, whilst in one it acted on the straw only; the phosphate in five cases affected the corn and straw, and in one the straw only. It seems then that nitrogen is available for barley in all localities, whilst phosphates or potash are less so. E. W. P.

Manuring Oats. By v. LIEBENBERG (*Bied. Centr.*, 1887, 651—653).—The experiments were conducted on the same principle and in the same manner as those on barley manuring. Nitrogen, and nitrogen combined with phosphate yielded an increase, but there is an uncertainty as to the gain produced by potash. Phosphates influence oats more than barley, because the former is slower and later in coming to maturity. E. W. P.

Comparative Experiments with Oats manured with Basic Slag on Moorlands. By BAESSLER (*Bied. Centr.*, 1887, 653—655).—The soil on which the experiments were conducted contained 69 per cent. organic matter, 2·7 N, 0·29 P₂O₅, and 13·66 per cent. ash. Kainite, basic slag, and superphosphates were used. Neither the super nor the slag produced any decided effects; kainite increased the yield of straw, but a general increase was remarked when the phosphates in either form were combined with kainite. The action of the slag was only 42 per cent. of that of the superphosphate, but this difference is compensated for by the lower price of the slag. E. W. P.

Manuring Winter Wheat and Winter Rye. By v. LIEBENBERG (*Bied. Centr.*, 1887, 656—658).—The manures were the same as those employed in the author's experiments on oats and barley. No decided nor especial advantage was remarked in the crop of wheat thus manured. As regards the rye, nitrogen alone produced no effect, but when combined with phosphates or kainite there was a very decided increase. The author accounts for the absence of effect

from the use of nitrogen by the fact that the land had previously received farmyard manure. E. W. P.

Manuring of Vines. By J. MORITZ and P. SEUCKER (*Bied. Centr.*, 1887, 604—609).—The experiments were instituted to determine if artificial manures could not be used for vines instead of the expensive farmyard manure. The manures were those usually employed, namely, ammonia superphosphates and potash compounds, and peat. The analyses of the must as well as its total quantity show that farmyard manure can be replaced by other manures; mineral manures seem to prevent the usual premature ripening, and consequently rotting, of some of the berries on the vines, whilst farmyard manure induces an extra growth of weeds. These experiments have been carried on for nine years, and are still being continued.

E. W. P.

Condition of Potassium in Soils, Plants, and Moulds. By BERTHELOT and ANDRÉ (*Compt. rend.*, 105, 833—840; 911—914).—1 kilo. of the dried earth contained 23·5 grams organic carbon, 1·66 gram nitrogen at the beginning of the season and 1·73 gram. and the end, and 8·92 grams of potassium. The only methods available for the estimation of the total potassium are those in which the soil is completely decomposed by ammonium fluoride, calcium carbonate, or barium hydroxide.

Water percolating through the soil removed only 0·0029 gram of potassium per kilo., but if the soil was treated with successive quantities of water the amount dissolved increased to 0·143 gram per kilo. Heating the soil to dull redness had little effect on the solubility of the potassium.

Ethyl acetate and ammonia have practically no effect on the solubility, but water containing 2 per cent. of sugar or acetamide dissolves more potassium compound than pure water. Water saturated with carbonic anhydride dissolved 0·198 gram per litre; water containing 2 per cent. of acetic acid dissolved 0·290 gram per litre; water with 2 per cent. of hydrochloric acid 0·404 gram; water with 2 per cent. nitric acid 0·296 gram. These results afford no definite evidence either as to the forms in which the potassium exists in the soil or as to the proportion assimilable by plants.

Concentrated hydrochloric and nitric acids at a higher temperature dissolve considerably more potassium, the exact quantity depending on the temperature and time of action. The whole of the potassium, however, is never removed. Calcination of the soil increases the proportion of the potassium soluble in acids, probably in consequence of some alteration of the silicates.

It is not possible to draw any sharp line of demarcation between the potassium which is soluble or insoluble, assimilable or non-assimilable.

In order to obtain similar information respecting the potassium present in living plants, *Mercurialis annua* was selected as an example. The dried plant contained per kilo. 19·35 grams of nitrogen and 27·87 grams of potassium oxide, and left 125 grams of ash.

When treated with 10 times its weight of water for 24 hours,

18.92 grams of potassium per kilo., or two-thirds of the total amount, was dissolved. Hydrochloric acid of 2 to 3 per cent. dissolved 24.58 grams of potassium in 24 hours, or 5.66 grams more than water. The remaining 3.29 grams was present in some form insoluble in dilute acids.

A sample of vegetable mould which was examined in a similar way contained 32.4 per cent. of water and lost 45.9 per cent. when calcined in presence of air. The dried mould contained per kilo. 95.8 grams of organic carbon; 14.5 grams combined carbonic anhydride; 8.6 grams of nitrogen; and 11.65 grams of potassium. 2.96 grams or one-quarter of the potassium was soluble in water; 5.84 grams was soluble in hydrochloric acid of 2 per cent., but even after incineration the quantity of potassium insoluble in acids was 2.14 grams per kilo. The proportion soluble in water was considerably less after incineration, owing doubtless to the action of the silicates on the potassium carbonate.

It is evident that the mould does not retain the whole of the potassium present in the original plant, a considerable proportion being removed by rain during the process of decay. The proportion remaining is, however, still much more considerable than in the soil, and mould is a truly complementary manure intermediate in its character between the organic and inorganic manures.

C. H. B.

Best Time for Ploughing Yellow Lupines under. By BAESSLER (*Bied. Centr.*, 1887, 615—618).—The periods into which the growth of the yellow lupine which was to be used as “green manure” was divided, were (1) full bloom of main stem, (2) commencement of podding of the same, (3) full bloom of side shoots, (4) full ripeness of the pods of main stem. It was found that the plants should be ploughed under in the fourth period, for then they would give to the morgen N 140.3 kilos., K_2O 53.96, and P_2O_5 25.7, when 253,440 plants are allowed per morgen; at this period, the nitrogen and phosphoric acid are three times and the potash twice that found in the plant in the period of bloom.

E. W. P.

Analysis of Rubbish-heaps employed to Improve Soils. By A. MAYER (*Bied. Centr.*, 1887, 577—578).—The rubbish-heaps are found at places of refuge which were frequented in times of flooding before Holland was protected by dykes; they consist largely of animal and vegetable remains. The analysis of one sample must here suffice: Organic matter, 6.0 per cent.; total nitrogen, 0.14; easily soluble nitrogen, 0.02; phosphoric acid, 0.78; potash, 0.34; calcium carbonate, 1.1. The material is richer in plant food than the various “muds” used for amelioration of poor land; in the former, the lowest quantity of phosphoric acid is higher than the highest percentage in the latter; the same may be said for potash and nitrogen, but the muds contain more calcium carbonate.

E. W. P.

Analytical Chemistry.

Support for Funnels while Drying. By V. MEURER (*Zeit. anal. Chem.*, **26**, 614).—Two horizontal, parallel bars of glass tube are supported by pieces of glass rod, which have their ends bent upwards till they nearly meet, and thrust into the ends of the tubes which are bent downwards at right angles. A small hook of glass rod prevents the bars from springing apart under the weight of the funnels which rest between them. M. J. S.

Moisture remaining in a Gas after drying by Phosphoric Anhydride. By E. W. MORLEY (*Amer. J. Sci.*, **34**, 199—204).—The method employed for determining the amount of aqueous vapour left in a gas after drying with phosphoric anhydride, consists in drying the gas with that substance, and then passing it through a weighed apparatus in which the gas is first slightly moistened, then much expanded, and, lastly, again dried by phosphoric anhydride. The decrease in weight of the apparatus is then due to the moisture left by phosphoric anhydride in that volume by which the gas passing out of the apparatus exceeds the gas entering it. In this way, it was found that the moisture left unabsorbed may be roughly estimated at a fourth of a milligram in 10,000 litres of gas. (For the result with sulphuric acid see Abstr., 1886, 278.) B. H. B.

Hygienic Air Analysis. By K. SONDÉN (*Zeit. anal. Chem.*, **26**, 592—598).—The apparatus is essentially that of Pettersson (Abstr., 1887, 999; also 179 and 180), but with the inlet tube so arranged as to draw the sample of air for analysis from a pipette in which it has been collected, thus avoiding the necessity of performing the analysis in the locality from which the air is taken. The carbonic anhydride only is determined, the gases being saturated with moisture before each measurement. Results agreeing closely among themselves and fairly with determinations by Pettenkofer's method have been obtained with an apparatus containing only 18 c.c. of air. M. J. S.

Estimation of Sulphurous Acid by Standard Iodine Solution. By J. VOLHARD (*Annalen*, **242**, 93—113).—The drawback to Bunsen's volumetric method, involving the use of standard iodine solution and dilute sulphurous acid, is the fact that the acid solution will not be completely oxidised if it contains more than 0.04 per cent. of SO_2 . The incomplete oxidation of the sulphurous acid in stronger solutions is generally attributed to the action of the sulphuric acid on the hydriodic acid: $\text{H}_2\text{SO}_4 + 2\text{HI} = \text{I}_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$. The author finds that the true explanation is, that sulphurous acid is decomposed by a strong solution of hydriodic acid, yielding sulphur and iodine; the iodine at once oxidises sulphurous acid to sulphuric acid and is itself converted into hydriodic acid; this secondary action may be avoided by adding the moderately dilute sulphurous acid to the standard iodine solution. W. C. W.

Rapid Method of Determining the Total Acidity in Flue Gases from Vitriol Chambers, adapted for the use of Workmen. By W. YOUNGER (*J. Soc. Chem. Ind.*, 6, 347—348).—The author recommends the use of Hurter's apparatus, which is described in detail in Wanklyn's book on "Gas Analysis." The method being intended only for the use of foremen, to serve as a guide in the working of chambers, no pretensions are made to any great degree of accuracy. The most useful property of the apparatus is that it indicates how far the combustion is carried on, what fuel is used, and how much is wasted.

D. B.

Soda-lime Method for Determining Nitrogen. By W. O. ATWATER and C. D. WOODS (*Amer. Chem. J.*, 9, 311—324).—The soda-lime is prepared by slaking $2\frac{1}{2}$ kilos. of lime in an iron kettle with a solution of 1 kilo. of sodium hydroxide, evaporating, and heating to fusion. It is ground whilst warm, and divided into two portions by sieves of $\frac{3}{4}$ mm. and 2 mm. This soda-lime is, on the whole, preferable to a more fusible one containing more soda, the complete decomposition of the substance being effected by the large surface presented by the coarse soda-lime with which the front part of the tube is filled. The same results are obtained whether the lime contains much or little soda, or even none, the ammonia probably being produced by the action of superheated steam. Combustions with sugar are not to be recommended for testing the purity of soda-lime, as even when recrystallised from alcohol it appears to contain a trace of nitrogen; stearic acid or oxalic acid is to be preferred. For the filling of the absorption-bulb, it is convenient to have a little thistle funnel blown on the end of the exit tube. If the tubes are well and closely packed with granular soda-lime, so as to leave no considerable open channel, and if a sufficiency of powdered soda-lime be well mixed with the substance, short tubes, 30 cm. long, may be used; cochineal is used as indicator.

When using the absolute method for the determination of nitrogen, a small correction should be made for the residual air and for the vapour-tension of the potash solution, namely, when at sp. gr. 1.36, 4 mm. at 9.5° and 6.5 mm. at 14.5°.

Although the results obtained by the two methods are almost the same, the soda-lime method is not quite so exact, but is much simpler, and sufficient for most purposes if the above precautions are observed.

H. B.

Determination of Nitrogen by Kjeldahl's Method. By L. LENZ (*Zeit. anal. Chem.*, 26, 590—592).—To ascertain whether the addition of permanganate is invariably necessary, comparative determinations were made on 11 nitrogenous substances, containing from 1.4 to 14 per cent. of nitrogen. In every case, the use of permanganate gave the higher result, the difference varying from 0.28 to 16 per cent. of the whole. The permanganate cannot, therefore, in any case be safely dispensed with.

M. J. S.

Apparatus for Nitric Acid Determination. By KRATSCHMER (*Zeit. anal. Chem.*, 26, 608—610).—A simple apparatus for Schlösing's method. A flask of 150 c.c. capacity is fitted with a caout-

chouc stopper, through which pass the tube of a separator bulb with a good stopcock and a long (3 to 4 dm.) delivery tube bent downwards at an acute angle and turned up at the end. The nitrate solution is boiled in the flask (the delivery tube dipping into the mercury trough) until every trace of air is expelled. The stopcock is then closed, a boiling hot mixture of ferrous chloride and hydrochloric acid is poured into the bulb, and the lamp is removed. As soon as the mercury begins to rise in the delivery tube, the ferrous solution is allowed to flow in, the lamp is replaced, and the nitric oxide boiled out as usual. A little of the ferrous solution should remain in the bulb to act as a seal. M. J. S.

Determination of Phosphoric Acid. By A. ISBERT and A. STUTZER (*Zeit. anal. Chem.*, **26**, 583—587).—The method based on the determination of the ammonia in the phosphomolybdate precipitate (Abstr., 1887, 526) is confirmed. A further simplification consists in washing the yellow precipitate with cold water instead of with ammonium nitrate solution. The compound of silicic acid with ammonia and molybdic acid is soluble in pure water although insoluble in ammonium nitrate. On the other hand, the phosphomolybdate requires 10,000 parts of cold water for its solution. The removal of silica by evaporation may therefore be omitted. The precipitate is allowed to subside completely at 70°, and filtered off after cooling. It is thrown with its filter into a flask, and distilled with soda into standard acid, which is then titrated back with baryta, using corallin as indicator. One part of nitrogen in the precipitate corresponds with 1.654 parts of phosphoric anhydride. Test analyses with known quantities of phosphate, with and without silicic acid, and comparative assays of phosphatic manures by the above and the gravimetric process, show that for commercial purposes the method is sufficiently accurate. M. J. S.

New Methods of Estimating Arsenic in Pyrites. By J. CLARK (*J. Soc. Chem. Ind.*, **6**, 352—355).—*Precipitation Process.*—Three grams of the finely powdered pyrites is mixed in a platinum crucible with four times its weight of calcined magnesia and soda, and the mixture heated for about 10 minutes over a moderately low Bunsen flame. The contents of the crucible are then extracted with boiling water and filtered. The filtrate, which should be green in colour owing to the presence of iron, is acidified with hydrochloric acid, and the solution, which is now nearly colourless, is boiled for a few minutes, when the arsenic sulphide will separate along with sulphur. To ensure complete precipitation of the arsenic, it is always advisable to saturate the solution with hydrogen sulphide. The precipitate is then thrown on to a filter, washed, dissolved with ammonia, and the solution evaporated to dryness on a water-bath. The residue is treated with nitric acid and the arsenic in the solution either estimated as magnesium ammonium arsenate, or precipitated as silver arsenate, and the arsenic calculated from the silver as determined volumetrically by Volhard's process, or gravimetrically by cupellation, as recommended by Richter.

Distillation Process.—About 1·7 gram of the finely pulverised pyrites is introduced into a platinum crucible with six times the weight of the above mixture, and heated for an hour over a low Bunsen flame. The contents of the crucible are transferred to a flask, moistened with water, and dissolved in strong hydrochloric acid. The flask, which is fitted with a funnel tube, having the end drawn to a point and dipping under the liquid, is then connected with a small glass condenser, to the end of which a straight calcium chloride tube is attached, and by means of the funnel tube a considerable excess of cuprous chloride dissolved in strong hydrochloric acid is introduced. The contents are then slowly distilled into water for an hour, when a fresh quantity of hydrochloric acid is introduced, and the distillation continued for $\frac{1}{2}$ hour. The whole of the arsenic will now be found in the receiver, but it is always advisable to add a little more hydrochloric acid, change the receiver, and test the distillate. The arsenic is then precipitated as sulphide, or it is titrated with iodine in the usual way.

D. B.

Estimation of Silicon in Iron and Steel. By J. J. MORGAN (*Chem. News*, 56, 221).—The author criticises Turner's statements (Abstr., 1887, 1140), and states that silica may be obtained free from iron and phosphorus in the following manner:—The solution obtained by dissolving iron in *aqua regia* is evaporated to a thick syrupy consistency, treated with hydrochloric acid, and the precipitated silica well washed with dilute hydrochloric acid and water, when it is found to be free from both iron and phosphorus.

D. A. L.

Estimation of Silicon in Iron and Steel. By T. TURNER (*Chem. News*, 56, 244—245).—A reply to Morgan (preceding Abstract). Whilst the process described above will give fairly accurate results with iron containing under 1 per cent. of phosphorus and about 1 per cent. of silicon, this is not the case with commoner irons containing 2 per cent. of phosphorus and 3 to 4 per cent. of silicon.

Indirect Determination of Alkalis in Presence of Lithium. By K. KRAUT (*Zeit. anal. Chem.*, 26, 604—605).—The metals are weighed as nitrates, and the nitric anhydride then expelled by fusion with silica. The calculation is made in the usual manner.

Chlorides are converted into nitrates by treatment with silver nitrate. Phosphates are dissolved in a little nitric acid, about an equivalent quantity of silver nitrate is added, and then freshly precipitated silver oxide to neutrality. The excess of silver in either case is removed from the filtrate by hydrocyanic acid. This method is not applicable to sulphates, since barium sulphate cannot be freed from lithium salts by washing.

M. J. S.

Determination of Ammonia in Commercial Products. By J. M. MILNE (*J. Soc. Chem. Ind.*, 6, 423).—Some time ago a German committee recommended the liberation of the ammonia from phosphates, manures, and other commercial products, by boiling with magnesia instead of alkaline hydroxides, and absorption in a measured

excess of standard sulphuric acid. One great advantage of this modification is that the contents of the distilling flask boil quite quietly, and can be brought nearly to dryness without spirting if the gas flame is properly regulated. The author has used this method for some time with very satisfactory results. It is necessary, however, to observe the following precautions:—(1) The steam containing the ammonia should be thoroughly condensed as it passes over. (2) The end of the condenser tube should not dip beneath the surface of the sulphuric acid in the bulb flask. (3) In order to ensure complete absorption of the ammonia, a small U-tube containing a little of the standard acid should be attached to the exit tube of the flask.

D. B.

Assay of Silver containing Small Quantities of Bismuth.
By J. SCULLY (see p. 108).

Estimation of Mercury in Urine. By L. BRASSE (*Compt. rend. Soc. Biol.* [8], 4, 297—300).—Simple electrolysis is insufficient, inasmuch as certain organic matters are deposited along with the mercury on the electrode. To obviate this error, the author treats 100 c.c. of urine with 10 c.c. of hydrochloric acid, places in the mixture a small coil of thin sheet brass 1 cm. broad by about 50 cm. long, and allows the interaction to go on for a day. The coil is then removed, washed with alcohol and ether, dried, transferred to a porcelain crucible and heated. The mercury vapour is condensed on a concave cover of gold kept cool by distilled water. The difference between the weight of the dried cover before and after heating gives the amount of mercury.

J. P. L.

Estimation of Iron in Chars. By R. DAVIDSON (*J. Soc. Chem. Ind.*, 6, 421).—Having tested the accuracy of the stannous chloride process for the estimation of iron in the case of substances such as animal charcoal, containing only from 0.1 to 1.0 per cent. of ferric oxide, the author confidently recommends it in preference to either the "permanganate" or "dichromate" process.

D. B.

Determination of Ferrous Oxide in Insoluble Silicates. By A. H. CHESTER and F. I. CAIRNS (*Amer. J. Sci.*, 34, 113—116).—In their examination of the crocidolite from Rhode Island, the authors determined the ferrous oxide by means of ammonium fluoride. Half a gram of the pulverised mineral is placed in a large platinum crucible over a water-bath, and a slow stream of carbonic anhydride is carried into it. When the air is expelled, a few drops of concentrated sulphuric acid is added, then some ammonium fluoride. Similar additions are made from time to time until the mineral is completely decomposed. The contents of the crucible are then emptied into a beaker containing cold water. The solution is diluted, and the iron determined by means of potassium permanganate in the usual manner.

B. H. B.

Estimation of Titanic Oxide. By L. LÉVY (*Compt. rend.*, 105, 754—756).—The author has investigated the conditions necessary to ensure accuracy when using the ordinary method of fusing with

potassium hydrogen sulphate, extracting with water, and precipitating the titanous oxide by prolonged boiling. The solution should contain 0.5 per cent. of free sulphuric acid; if less, the precipitate is impure; if more, precipitation is incomplete. The presence of zinc in the solution is without influence on the result, provided the proportion of free acid is 0.5 per cent., and the same is true of copper, magnesium, and aluminium, but in presence of ferric sulphate the result is always too high.

The best method of procedure is as follows:—The fused mass is mixed with sufficient sulphuric acid to convert the whole of the potassium into the hydrogen sulphate, solution being thus greatly accelerated, and the liquid is then carefully neutralised with potassium hydroxide, free sulphuric acid added to the extent of 0.5 per cent., and the solution boiled for six hours.

C. H. B.

Determination of Antimony. By F. MUCK (*Zeit. anal. Chem.*, **26**, 600—602).—The precipitate of trisulphide is dried by suction until it can be detached from the filter. The filter is washed with warm ammonium sulphide in which much free sulphur has been dissolved, this polysulphide having a far greater solvent action than the monosulphide. The solution is evaporated in a porcelain crucible. A convenient way of doing this is to support the crucible on a glass triangle in a deep glass basin containing a little sulphuric acid, and covered closely with a glass plate. On gently heating the basin on a bed of asbestos, the liquid evaporates rapidly without spitting. The detached precipitate is then added and the whole dried. The free sulphur is removed by treatment with a mixture of carbon bisulphide and chloroform, and the antimony sulphide is converted into tetroxide for weighing.

M. J. S.

Delicate Test for Bismuth. By F. B. STONE (*J. Soc. Chem. Ind.*, **6**, 416).—This test depends on the fact that a strong solution of potassium iodide produces a bright yellow colour when added to a very dilute solution of bismuth sulphate containing only a small quantity of free sulphuric acid. 1 part of bismuth oxide in 1,000,000 parts will show a distinct coloration. Very small quantities of bismuth may also be estimated colorimetrically by means of this test.

D. B.

Detection of Nitrates in Well Water. By O. BINDER (*Zeit. anal. Chem.*, **26**, 605—606).—The method depending on the reduction to nitrite by zinc, and testing with potassium iodide and starch, fails if too much zinc is used. A trace of zinc powder shaken with the liquid answers better than compact zinc.

M. J. S.

Water Analysis. By O. BINDER (*Zeit. anal. Chem.*, **26**, 607).—Liquids, such as natural waters, evaporated over a free gas flame, become contaminated with sulphuric acid from the products of combustion.

M. J. S.

Elementary Analysis of Highly Volatile Organic Liquids. By G. KASSNER (*Zeit. anal. Chem.*, **26**, 588—590).—The combustion

tube is prolonged at the posterior end beyond the furnace, and is bent upwards at an angle of about 45° . A plug of asbestos is placed at the bend. The bulb containing the liquid is introduced at this end, and rests against the asbestos plug with its capillary tube pointing upwards. The bulb having been cooled before breaking the point of the capillary tube, can be introduced without the escape of any of the liquid, and the gradual expulsion of the contents can be watched and regulated, since the vaporised liquid condenses in the capillary tube, and is driven out in the form of minute drops. These are immediately evaporated and swept forward by the current of oxygen passed through the tube. The more volatile the liquid, the longer and narrower should be the capillary tube. The portion of the combustion tube which is to be heated is filled with platinised asbestos (see Kopfer, *ibid.*, 17, 1). For substances which burn with difficulty, however, cupric oxide cannot be dispensed with. For arresting halogens, a plug is employed prepared by shaking chopped asbestos with finely divided, reduced silver. A stream of hydrogen (free from arsenic or antimony) passed through the hot tube regenerates the metallic silver after it has absorbed a halogen. M. J. S.

The Stalagmometer. By J. TRAUBE (*Ber.*, 20, 2824—2835).—Applications of the stalagmometer (this vol., p. 91) to the estimation of alcohol in wine, beer, and liqueurs, and of acetic acid and alcohol in vinegar. Tables are given for use at temperatures between 10° and 30° for alcohol, and 11° and 29° for acetic acid, for percentages up to 10 per cent. by weight of the pure substance in each case.

W. P. W.

Recognition of Pyrogallol. By G. KLIEBAHN (*Zeit. anal. Chem.*, 26, 641).—Pyrogallol when fused with ammonium oxalate yields ammonium rufigallate, which dissolves in water with red colour, and gives the following characteristic reactions:—Potassium ferrieyanide and potassium dichromate, a dark-brown precipitate insoluble in alcohol. Ferric chloride, no black coloration. A few drops of acetic acid, then potassium cyanide and mercurous nitrate, a black precipitate. Sodium nitroprusside and platinic chloride, no precipitate or change of colour. Potash, a change to brown, but not to black.

M. J. S.

Estimation of Grape-sugar in Urine by Robert's Method. By V. BUDDE (*Pflüger's Archiv*, 40, 137—172).—The fermentation method of determining the amount of sugar in diabetic urine consists in multiplying the difference in specific gravity before and after removal of the sugar by fermentation, by a constant factor found by control titration experiments in which the percentage so found was divided by the difference in the specific gravities. Worm-Müller has stated (*ibid.*, 37, 479—510) that this factor is constant, namely, 230. This paper is devoted to showing mathematically that from its very nature this factor is a variable one, increasing as the percentage of sugar diminishes.

W. D. H.

Examination of Wort and Starch. By E. W. T. JONES (*Analyst*, 12, 163—168).—The methods employed are essentially those described by O'Sullivan (this Journal, 1876, ii, 130). An analysis is given of a wort which gave $[\alpha]_{D-66} = 116.5$, and $K = 50.8$ (Trans., 1879, 606). The same wort analysed in the Inland Revenue Laboratory gave the values $[\alpha] = 120$, and $K = 57.2$, on which numbers a charge of the addition of 1.6 per cent. of glucose was based. The suggestion is made that the higher value of K may have been obtained by the use of Fehling's solution volumetrically in the presence of dextrin. On keeping this wort for four months (after adding salicylic acid), the rotatory power diminished, whilst the cupric reducing power increased. Some of the same malt, mashed in the laboratory for three hours at $57-60^\circ$, gave $[\alpha] = 113.6$, $K = 51.85$, from which it would appear that with some malts the limits recognised by the Inland Revenue chemists ($[\alpha]$ not less than 120, and K not over 51) may be exceeded.

The method of analysing starch differs from that of O'Sullivan (Trans., 1884, 9) only in the omission of the washings with ether, alcohol, and warm water before gelatinising, and in controlling the results of the optical method by a subsequent hydrolysis with acid, and a determination by Fehling's solution. M. J. S.

Estimation of Small Quantities of Lactic Acid. By W. WINDISCH (*Chem. Centr.*, 1887, 826, from *Wochenschr. f. Brauerei*, 13, 214).—In order to estimate small quantities of lactic acid, the substance to be examined is heated with chromic acid, whereby the lactic acid is decomposed into formic acid and aldehyde. The mixed vapours are passed into Nessler solution, in which, in presence of an aldehyde, lead salts give a yellowish-red precipitate, or with smaller quantities, a yellowish opalescence. In order to examine roots by this process, they are first extracted with ether, which dissolves out all acid substances. V. H. V.

New Method of Examining Butter. By T. T. P. B. WARREN (*Chem. News*, 56, 222, 231, 243—244).—Five grams of butter is placed in a tared tube, plugged with asbestos, and is extracted with carbon bisulphide. The fats are weighed, dissolved in carbon bisulphide, and well mixed with a solution of equal volumes of yellow sulphur chloride and carbon bisulphide; the latter is evaporated, and the thickened mass redissolved in carbon bisulphide, any insoluble residue indicating the presence of vegetable oils. The filter tube is dried and weighed; then by successive weighings after washing, first with water, then with ammonia, the dry matter, soluble substances, casein, &c., are determined. The sulphur chloride treatment applied to other fatty mixtures, such as lard, oil, or oleomargarin, will detect the admixture of any vegetable oil, rosin, rosin oil, or petroleum. After a few hours' contact with sulphur chloride, butter becomes brownish, commercial olein thickens and turns black, and animal olein assumes a very dark colour, but all dissolve in carbon bisulphide, whereas vegetable oils do not. Inasmuch as animal oils themselves dissolve vegetable oils, a small quantity of the latter might

escape detection in presence of a large quantity of the former; to avoid this it is suggested to add to the butter or other fatty mixture sufficient tested cotton-seed oil to supersaturate the animal fats; then by treatment with sulphur chloride and subsequent washing with carbon bisulphide, the animal fats are removed, and the vegetable oils remain insoluble. Any excess residue over that due to the cotton-seed oil added is derived from vegetable oil present in the butter; this is, however, only approximately quantitative. Water must be absent when using sulphur chloride. Other precautions are noted, and some remarks are advanced on the character of the reaction of sulphur chloride on fats, and of the products formed in the reaction. Attention is drawn to the high percentage of casein in some samples of country butter, probably indicating the use of this substance as an adulterant.

D. A. L.

The Reichert-Meissl Process for the Estimation of Butter Fat. By R. WOLLNY (*Bied. Centr.*, 1887, 699—703).—Errors frequently arise in the results obtained by working this process, the results being generally too high. This the author ascribes to the presence of carbonates in the potash used for saponification. A loss may also occur from the fact that distillation with sulphuric acid in presence of alcohol will produce ethereal salts of butyric and other acids, consequently the results may be too low. If the following precautions are taken, the results will be accurate. Instead of potassium hydroxide, a 50 per cent. sodium hydroxide solution is to be used, and allowed to settle before putting aside. Admission of carbonic anhydride to the saponifying solution must be avoided, and for this purpose the saponification must be conducted in a vessel to which a reflux condenser is attached, and the distillation of the alcohol should be effected without opening the apparatus. A closed T-tube is inserted between the flask and condenser, whereby, after distillation, water and acid can be added. As regards the process itself, 5 grams of the molten and filtered fat is accurately weighed into a 300 c.c. flask (length of neck 7 to 8 cm.), 2 c.c. of 50 per cent. sodium hydroxide solution, which has been preserved from all contact with carbonic anhydride, and 10 c.c. alcohol (96 vol. per cent.) are introduced into the flask, and after connection with the reflux condenser the flask is heated in the water-bath for $\frac{1}{4}$ hour; the alcohol is distilled off, and the heat continued for at least $\frac{1}{2}$ hour, 100 c.c. distilled water is then added, and the mixture further heated for $\frac{1}{4}$ hour, until the soap is dissolved. The clear solution is now to be decomposed whilst hot by 40 c.c. of sulphuric acid (30—35 c.c. = 2 c.c. of the soda solution), and a small piece of pumice should also be introduced. Distillation must be continued until 110 c.c. of the liquid has been collected, the distillate well mixed, and of it 100 c.c. filtered off and titrated with decinormal baryta, phenolphthalein being used as indicator. The figure thus obtained is to be multiplied by 1.1, and from the product are to be deducted such figures as are obtained from a preliminary blank experiment. The deduction to be made should not exceed 0.33.

E. W. P.

Examination of Cod-liver Oil and Vegetable Oils. By E. SALKOWSKI (*Zeit. anal. Chem.*, **26**, 557—582).—The determination of the temperature of solidification is of little assistance, since undoubtedly genuine specimens show widely different solidifying points. Moreover, cod-liver oil solidifies with extreme slowness, even at temperatures far below its freezing point, and an admixture of 20 per cent. of rape-seed, linseed, or cotton-seed oil, with an oil of low freezing point is not revealed at a temperature (0° C.) at which other genuine oils solidify. The presence of palm oil, palm kernel oil, or cocoa-nut oil may, however, be suspected if solidification occurs in 15 to 30 minutes at 0° .

Treated by Reichert's process, cod-liver oil gives a very small quantity of volatile acid. Linseed, rape-seed, cotton-seed, and palm oils give a slightly higher yield, but not sufficiently different to enable this method to detect an admixture.

When cod-liver oil is saponified and the dilute solution of the soap shaken with ether, cholesterin is extracted, together with a yellow substance, which seems to belong to the lipochrome series (Kühne, *Untersuch. physiol. Inst. Heidelberg*, 1882). This substance gives an indigo-blue colour with strong sulphuric acid, whilst cholesterin and also the cod-liver oil itself give violet. The fatty acids from the soap solution freed from cholesterin, when dissolved in chloroform and mixed with sulphuric acid, give a dark brown-red colour, with dirty-green fluorescence. If after pouring off the chloroform some of the acid is added to glacial acetic acid, the mixture slowly acquires a fine red-violet colour, with dirty-green fluorescence. The only vegetable oils which in chloroform solution are coloured blue by sulphuric acid are palm oil and cotton-seed oil. All the vegetable oils (except palm oil), when treated as above for the extraction of cholesterin, yielded a substance which was identified with the phytosterin of Hesse. This may be distinguished from cholesterin by its appearance under the microscope. A hot alcoholic solution of cholesterin solidifies on cooling to a mass of thin, rhombic plates, frequently showing re-entering angles; the substance obtained from the vegetable oils forms stellate or fasciculate groups of thick needles, or on slow cooling gives elongated six-sided plates. The products from all the vegetable oils melted at 132 — 134° (Hesse's phytosterin at 132 — 133°). Cholesterin from genuine cod-liver oil melts at 146° ; the product from an oil adulterated with 20 per cent. of rape, linseed, or cotton-seed oil melted at 139 — 140° , and showed the needles of phytosterin, together with the plates of cholesterin.

Most of the specimens of cod-liver oil examined contained very little free fatty acid (0.24 to 0.69 per cent. calculated as oleic acid; one specimen, however, showed 6.5 per cent.). Since many vegetable oils give numbers lying within these limits, this character is of no service for their detection.

M. J. S.

Titration of Urea with Mercuric Nitrate. By E. PFLÜGER (*Pflüger's Archiv*, **40**, 533—586).—After some critical remarks on von Rautenberg's and Pfeiffer's modifications of Liebig's method of estimating urea, a series of 28 experiments is detailed, in which

the amount of nitrogen in urine was estimated first by Kjeldahl's method, and secondly by Rautenberg's mercurial solution. In some cases, the results by the latter were higher, in others lower than by Kjeldahl's method, and taking Kjeldahl's method as one which gives accurate results, it is calculated that the average error of Rautenberg's method is 0.7 per cent. On the average, out of 100 parts of the nitrogen in urine, 13 are combined in substances other than urea. Rautenberg's method does not give the amount of urea, but the total nitrogen.

W. D. H.

Fractional Reduction of Ortho- and Para-nitrotoluene and Quantitative Analysis of Ortho- and Para-toluidine. By T. MINIATI, H. BOOTH, and J. B. COHEN (*J. Soc. Chem. Ind.*, **6**, 418—420).—From a series of experiments on the reduction of ortho- and para-nitrotoluene, it seems that both nitro-compounds are acted on concurrently.

Before commencing their analytical work, the authors thought it desirable to determine whether the reduction could be so regulated that approximately the same quantities of nitrotoluene could be reduced with a given quantity of the reducing agent; it was found that with care this could be readily accomplished. The separation and isolation of the nitrotoluene and toluidine is effected in the following manner:—After reduction, the acid solution obtained is distilled with steam, and the unattacked nitrotoluene driven over, the toluidine remaining behind. The toluidine solution is freed from tin by treatment with hydrogen sulphide and filtered. The filtrate is made alkaline and distilled with steam, when the toluidine distils over. Both distillates are extracted with ether, the ether is distilled off and the residues dried and weighed. The first gives the weight of nitrotoluene, the second that of the toluidine. Having the respective weights, an analysis of the one or the other and determination of the quantity of ortho- and para-compound present therein, suffices to find exactly how the reduction has gone. Having made unsuccessful attempts to analyse the resulting nitro-compound, the authors tried various methods for the quantitative estimation of ortho- and para-toluidine. The only process they found practicable was to add excess of oxalic acid solution, bring the precipitate on to a filter-paper, wash three or four times with ether, and weigh on a watch-glass. Any residue remaining in the precipitating vessel and in the filter-paper was dissolved in water and titrated with decinormal potash solution. With paratoluidine, it was found that precipitation was not complete unless the mixture was allowed to remain 12 hours. With pure orthotoluidine, there is no immediate precipitation, but in 12 hours from 4 to 5 per cent. of the ortho-compound crystallises out; hence in performing the analysis the error due to the precipitation of the ortho-compound must be allowed for if the solution remains 12 hours, or the error due to incomplete precipitation of the para-compound must be allowed for if the precipitate is filtered immediately. The better plan would therefore be to obtain an approximation of the amount of para-compound present in one determination,

and then run in just sufficient oxalic acid solution to precipitate this quantity, and wait for 12 hours. D. B.

Estimation of Small Quantities of Paratoluidine in Orthotoluidine. By C. HÆUSSERMANN (*Chem. Ind.*, 10, 55–56).—Of the methods recommended for the estimation of para- and ortho-toluidine the process based on the titration of the para-compound with oxalic acid in an ethereal solution has been mostly adopted. It is not, however, wholly free from error, owing to the fact that the amount of ether to be used is frequently insufficient to completely dissolve the “ortho-oxalate” produced by the reaction. The author suggests the following method:—A solution containing 88 grams of crystallised oxalic acid in 750 c.c. of water and 43 c.c. of hydrochloric acid of 22° B. is heated in a porcelain basin to 70–75°, and treated with 10 grams of the toluidine under examination. When the precipitate which separates has been entirely redissolved, the mixture is allowed to cool gradually to 30–35° until the oxalate shows signs of crystallisation on the surface of the solution. It is then filtered through cotton and the residue washed with a few drops of water. The precipitate forms small, colourless scales having a dull appearance. The filtrate on standing deposits a further portion of crystals which are collected on a separate filter and washed. This operation is repeated until crystals are obtained having a lustrous appearance. These consist of the pure “ortho-oxalate,” and are readily distinguished from the crystals of the para-compound. The crystalline fractions are then treated with a solution of sodium carbonate and subjected separately to distillation. The solidifying point of the distilled bases is determined by cooling a fraction of each distillate with ice. If the oil solidifies by merely agitating it, the crystals are collected on a tared filter, and after drying over sodium hydroxide weighed as paratoluidine. If, however, the addition of a few crystals of pure paratoluidine is required to induce solidification, only one-half of the mass is calculated as paratoluidine. If, on the other hand, it is impossible to solidify the base obtained from the distillation of the first crystalline fraction, orthotoluidine only is present in the sample under examination. With good toluidines, it generally suffices to collect and distil two fractions, in which case the base from the second crystallisation mostly constitutes a perfectly liquid oil. This method being inapplicable to mixtures containing more than 10 per cent. of paratoluidine, it is suggested to dilute such mixtures by the addition of pure orthotoluidine. D. B.

Volumetric Determination of Alkaloids by Mayer's Reagent. By F. S. HERETH (*Zeit. anal. Chem.*, 26, 647).—To avoid the errors introduced by the use of filters and the irregular addition of the reagent (potassio-mercuric iodide), several equal portions of the solution to be titrated should be mixed at once with quantities of the reagent differing from one another by 0.1 c.c., and ranging from somewhat below the amount indicated by a rough preliminary test to an equal distance above. After settling for at least eight hours in a

closed test-tube, part of the clear upper liquor can be poured off and tested by a drop of the reagent. The extract is prepared for titration by acidifying and gently warming to drive off alcohol. If any precipitate separates it is filtered off and washed with dilute acid. The liquid should finally contain about 1 per cent. of free sulphuric acid.

M. J. S.

Tanret's Reaction for Albumin, Peptone, and Alkaloids in Urine. By L. BRASSE (*Compt. rend. Soc. Biol.* [8], 4, 369—370).—Albumin, peptone, and alkaloids are precipitated from urine in the cold by Tanret's reagent, potassium mercury iodide. On heating, the peptone and alkaloidal precipitate dissolves, leaving the albumin insoluble. The alkaloidal precipitate can be easily separated from the peptone precipitate by reason of its solubility in ether.

No insoluble combinations are formed with any of the ordinary constituents of urine, such as creatine, creatinine, xanthine, or hypoxanthine, but bile salts give rise to a precipitate insoluble, like albumin, in both cold and hot solutions. This precipitate, however, can be differentiated from the ordinary albumin precipitate inasmuch as it is soluble in ether.

J. P. L.

Hæmatoscopic Study of Blood. By A. HÉNOUQUE (*Compt. rend. Soc. Biol.* [8], 4, 283—284).—The chief advantage in the use of the hæmatoscope (Abstr., 1887, 312), for the spectroscopic examination of blood is the possibility of examining the blood undiluted.

J. P. L.

General and Physical Chemistry.

Chemical Action of Light on an Explosive Mixture of Chlorine and Hydrogen. By E. PRINGSHEIM (*Ann. Phys. Chem.* [2], 32, 384—428).—Bunsen and Roscoe (*Ann. Phys. Chem.*, 96, 373; 100, 43, 481; 101, 235; 108, 193; 117, 529) propounded the question—"Whether in photochemical combination an amount of work is done for which an equivalent of luminous energy disappears, or whether the action effected by the chemical rays is merely started by the light without the expenditure of a sensible amount of luminous energy." They endeavoured to solve this problem in the case of hydrogen and chlorine, by comparing the quantity of light absorbed by the mixture with that absorbed by dry chlorine, or as they call it, the optical extinction in chlorine. They assumed that this optical extinction would be of the same amount in the mixture, and therefore concluded that the considerable additional extinction observed in the mixture was due to the transformation of luminous energy into heat energy during the chemical action. The author objects to this reasoning, that the light absorbed in chlorine alone is itself transformed into heat, thereby raising the temperature of the gas, whilst in the case of the mixture, the luminous energy may very probably be transformed directly into chemical energy. In support of this view, he adduces Bunsen and Roscoe's observation that the action of light was considerable when the range of temperature was from 18° to 26°.

The luminous energy, indeed, may either increase the molecular motion directly and the atomic motion indirectly, or *vice versa*, or more probably both processes may go on simultaneously. From the kinetic theory of gases, the introduction of energy by conduction of heat must increase the molecular velocities, which are of a very irregular character. Now it is found that the absorption of light is a function of the wave-length, and it therefore seems probable that the chemical action of light consists in the direct transfer of energy to the atoms, whose motions consist of vibrations of definite periods, and is therefore the direct cause of dissociation. When in equilibrium, there is a definite relation between the atomic and the molecular energy of a gas, and if this is disturbed by the absorption of light, there will be a change in the number of molecular impacts, and before a fresh state of equilibrium is attained, the direct increase in the atomic energy may be more or less expended; in the present case in effecting chemical change; in other cases, in producing fluorescence, phosphorescence, or electrical phenomena. The assumption, therefore, that what Bunsen and Roscoe call the optically absorbed light simply increases the temperature, and that the additional absorption due to the presence of hydrogen increases the chemical absorption, is not justifiable. If the light absorbed by the chlorine molecules in the mixture produces chemical action, this, as shown later, will probably

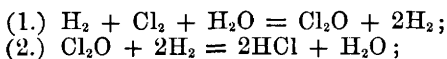
consist in the formation of intermediate unstable products whose coefficient of absorption of light differs from that of the mixture of chlorine and hydrogen, so that "chemical extinction" must be regarded as the consequence rather than the cause of the chemical change. The existence of chemical extinction is therefore no criterion as to whether transformation of luminous into chemical energy takes place, so that Bunsen and Roscoe's method is incapable of solving the question proposed by them, but a result obtained in another portion of their researches, namely, that the chemical action is proportional to the intensity of the light, although not so applied by them, seems to give the required solution; for if the action of the light were simply to disturb a state of unstable equilibrium, the quantity of hydrogen chloride formed would be independent of the initial impulse. It must, therefore, be assumed that a definite absorption of luminous energy will take place for every molecule of hydrogen chloride formed, but it does not follow that more light must be absorbed than with the chlorine alone.

The determination of the cause of the increase of the extinction-coefficient, which may be due merely to a change in the condition of the mixture, leads to an investigation of the physical and chemical phenomena which accompany the formation of hydrogen chloride, and therefore to the consideration of "Photochemical Induction." Bunsen and Roscoe found that when light falls on a freshly prepared mixture, or on one which has been for a time in darkness after previous exposure to light, there is at first no appreciable formation of hydrogen chloride; after a certain interval, a slight action begins, gradually increases to a maximum, and then remains constantly proportional to the time. The act of overcoming the resistance here indicated and bringing the gas into a state of readiness for combination, they call chemical induction, and when due to the action of light, photochemical induction. They found the duration of the seemingly inactive interval to increase with the thickness of gas traversed by the light, and to decrease with increasing intensity of light more rapidly than the intensity increases. Both of these results are confirmed by the author, who further finds that the rate of formation of hydrogen chloride depends only on the intensity, and not on the wave-length of the light, from which he concludes that the inductive action is probably a chemical one. By instantaneous exposure to a stronger source of light, he finds that the gas undergoes a momentary expansion proportional to the intensity of the light, which is evidently not due to the heat of formation of hydrogen chloride, from the rapidity with which it appears and disappears, and also because it is found to be independent of previous induction and of the amount of hydrogen chloride formed. Neither can it, for the former reason, be due to the heat which Budde (*Ann. Phys. Chem.*, **144**, 213) has shown to be produced by the absorption of light by chlorine.

He therefore concludes that some intermediate product is formed, that the expansion is due to momentary dissociation, and that the quantity formed is proportional to the intensity of the light. It does not seem reasonable to suppose that this may consist of molecules of H_2Cl and Cl or HCl_2 and H ; the author therefore seeks for the cause in

the presence of water-vapour (the gas being in contact with water during the experiments), in accordance with the influence known to be excited by water-vapour on other explosive mixtures, and in confirmation of this he finds that when a solution of hydrogen chloride is substituted for the water, and the gas dried as completely as possible, much less hydrogen chloride is formed by the action of light of given intensity, and with the feeble light used in the earlier experiments, no action at all takes place.

The author assumes the action to take place in two stages, for example:—



or some similar action, the exact nature of which may be determined by chemical analysis. He supposes the action to be somewhat as follows:—The intermediate substance is first formed, the process continuing until a certain proportion of the gas is transformed. Mass actions then come into play between chlorine, hydrogen, water and the intermediate product, and hydrogen chloride begins to be formed. The second stage of induction now begins. The amount of the intermediate product increases more rapidly than it is used up in forming hydrogen chloride, which is therefore formed at an increasing rate, until the intermediate product is destroyed as fast as it is produced, introducing the third stage, in which the formation of hydrogen chloride is proportional to the time. When removed from the action of light, the quantity of intermediate product will soon fall below the minimum required for the production of hydrogen chloride, and the remainder will break up again into hydrogen, chlorine, and water. This gradual decomposition of the intermediate product into its original constituents will go on even during induction, which explains why, with diminishing intensity of light, the duration of induction increases more rapidly than the intensity diminishes, for since the nature of the change undergone by the intermediate product depends on its actual amount, therefore the less the intensity the greater will be the ratio of the amount destroyed to that newly formed in each moment.

G. W. T.

Anomalous Dispersion produced by Glowing Vapours. By A. WINKELMANN (*Ann. Phys. Chem.* [2], **32**, 439—442).—Kundt (*Ann. Phys. Chem.* [2], **10**, 231) discovered the anomalous dispersion produced by sodium vapour. The method he used was to allow a ray of light to pass through the conical flame of a Bunsen burner coloured with sodium vapour, so as to be refracted by the flame, which acted like a prism with its refracting angle horizontal and upwards, and then through a vertical prism, by which means he obtained crossed spectra which showed the anomalous dispersion. In the hope of making the action stronger, Kundt attempted, but without success, to reduce the flame to a prismatic form by the use of glass or mica plates. The author has succeeded in doing this by using as the burner a tube of triangular section and provided with an air-blast.

On the top of the tube is placed a double thickness of wire-gauze, and on that again a triangular support smaller than the section of the burner, made of iron wire, which carries an iron cup of the same dimensions as the support, in which the sodium is placed.

With this apparatus Kundt's phenomenon was exhibited very clearly, and it was also obtained, although less distinctly, with potassium. Lithium and thallium chlorides were also tried but with negative results; this the author attributes to the insufficient density of the vapour.

G. W. T.

Components of the Rare Earths yielding Absorption-spectra.

By G. KRÜSS and L. F. NILSON (*Ber.*, **20**, 3067—3072).—A reply to G. H. Bailey (this vol., p. 1), in which the authors maintain the correctness of their views on the components of the rare earths (*Abstr.*, 1887, 890).

Components of the Rare Earths yielding Absorption-spectra.

By G. H. BAILEY (*Ber.*, **20**, 3325—3327).—A rejoinder to the preceding Abstract.

Theory of Researches on Contact-electricity. By F. EXNER (*Ann. Phys. Chem.* [2], **32**, 515—520).—The author's recent researches in support of his denial of contact-electrification (*Ann. Phys. Chem.* [2], **32**, 53) were founded on his experimental result, that if an insulated conductor is connected with an electrometer, and the latter then disconnected from the earth, and if the capacity of the conductor is then altered, the electrometer will remain unaffected, whilst according to the contact-theory there should be a flow of electricity.

The present note is a reply to objections which Hallwachs (*ibid.*, 64) has advanced against the author's conclusions.

In reply to these objections he states that—

(1.) The potential of the grating of oxidised iron which surrounded the apparatus differed by less than 0.05 of a Daniell from that of the walls of the room, which would justify his neglecting it; moreover, from (4), its potential, whatever its value, would be without influence on the results.

(2.) The capacity of the conductor was measured inside the grating, and not outside as assumed by Hallwachs.

(3.) He is justified in neglecting the change of capacity in the quadrants during the movement of the needle, since for the maximum deflection to be expected the error so arising would not exceed 1 per cent., and as no deflection was observed, the objection is entirely irrelevant.

(4.) The potentials would naturally be understood to refer to that of the grating as zero, without an express statement to that effect; moreover, the author shows by a simple mathematical proof that the result is independent of the absolute values of the potential, the essence of his method consisting in eliminating the influence of the grating by comparative observations on different metals. The difference of deflections which should have been obtained according to

the contact-theory would have amounted to from 10 to 15 scale-divisions, and would therefore be easily observed.

(5.) To eliminate the possibility that the absence of a deflection might be due to unknown external effects, a Daniell's cell was introduced into the insulated system, and the deflection obtained was found to agree closely with the value predicted theoretically.

(6.) The author claims that he has proved that no change is produced when the grating is brought into contact with a conductor consisting of a different metal. Such a change is required by the contact-theory, but the author has not attempted to determine whether it would be required by the chemical theory, nor, as far as he is aware, has the question been considered by others. G. W. T.

Resolution of the Electromotive Forces of Galvanic Elements into their Differences of Potential. By J. MOSER (*Monatsh.*, 8, 508—509.)—Examples are given in this paper of the resolution of the electromotive forces of certain galvanic combinations, and determination of each of the components at the electrolytic surface. The sum of these several components is shown to be equal to the total electromotive force of the cell. The method of "drop electrodes," as applied by the author to exclude the electromotive force of contact metals, is used, a method based upon an observation of Helmholtz, that if an insulated mass of mercury, dropping quickly, is in contact with an electrolyte at the dropping point, there is no difference of potential between the mercury and the electrolyte.

Thus the total electromotive force of the combination $\text{Zn} \mid \text{dilute ZnCl}_2 \mid \text{concentrated ZnCl}_2 \mid \text{Zn} = 0.15$ volt. The values of the electromotive force at the three surfaces v , f , and c , were found by the drop electrode method to be—

$$\begin{aligned} v &= 1.1 \text{ volt} \\ c &= 0.98 \text{ and } f = 0.27 \\ f + c &= 0.95. \end{aligned}$$

Now $1.1 - 0.95 = 0.15$, or the value found for the total electromotive force.

Again taking the Daniell's cell as another example—

$$\left. \begin{array}{l} \text{Zn} \mid \text{ZnSO}_4 \\ \text{Zn} \mid \text{ZnSO}_4 \mid \text{CuSO}_4 \\ \text{Cu} \mid \text{CuSO}_4 \end{array} \right\} \begin{array}{l} = 198 \\ = 232 \\ = 40 \end{array} \left. \begin{array}{l} \\ \\ \end{array} \right\} \begin{array}{l} \text{total electromotive force} = 232 - 40 \\ = 192, \end{array}$$

a value agreeing with that obtained by direct observation. A similar agreement between the sum of the differences of potential and the total electromotive force in the Latimer-Clark's cell is also noticed.

V. H. V.

Property of the Alkalis of increasing the E.M.F. of Zinc. By J. H. KOOSEN (*Ann. Phys. Chem.* [2], 32, 508—515).—Grove, Joule, Poggendorff, and others have observed the increased E.M.F. obtained by substituting aqueous potash or soda for the dilute acid in a cell. The author states that according to his researches the alkali, say potassium hydroxide, has a four-fold action: (1) it breaks up

into potassium and oxygen; (2) potassium replaces zinc in its electrical action, for instance, in a Daniell's cell potassium sulphate is formed in place of zinc sulphate, as the copper is deposited; (3) the zinc is oxidised by the oxygen of the potash; (4) the resulting zinc oxide is dissolved by the aqueous potash. (1) Diminishes the E.M.F., whilst (2) and (3) increase it; (4) may possibly slightly increase it, but it would be desirable to have positive evidence on this point.

If the external resistance of a cell is very great, almost the whole heat of combination will be developed in the external circuit. Let the E.M.F. of a Daniell's cell be taken as the unit of E.M.F., and let the unit of heat be the amount generated in a Daniell's cell by the decomposition of n grams of zinc, where n is the atomic weight of that metal. Then from Thomsen's determinations, the E.M.F. of a Daniell's cell is given by the equation $\text{ZnSO}_4(248) - \text{CuSO}_4(198) = 50 = 1$ Daniell; and with potash substituted for dilute sulphuric acid, $\text{K}_2\text{SO}_4(337) + 2\text{ZnOH}_2\text{O}(166) - 2\text{KHO}(232) - \text{CuSO}_4(198) = 73 = 1.46$ Daniell. For the author's zinc-bromine-platinum cell, $\text{ZnBr}_2(91) = 1.82$ Daniell.

The results thus theoretically obtained in the case of these and a few other simple cells considered by the author agree closely with experimental determinations. The heat of combustion of zinc oxide and potassium is not taken into account, as it is certainly not more than 2 per cent. of that due to the decomposition of zinc in a Daniell's cell, and according to Favre and Silbermann it would seem that the chemical action is merely local, and does not contribute to the electrical energy. Practically the author finds that a Daniell's cell with a solution of potassium hydroxide is very satisfactory for giving continuous currents through a high resistance, and sodium hydroxide gives still better results, as sodium sulphate, being more soluble, does not so readily crystallise on the porous cell.

It is very important to prevent interdiffusion of the fluids as far as possible, and for this purpose the author uses a double porous cell, having the intermediate space filled with a solution of potassium and sodium sulphates respectively, with a small admixture of sulphuric acid to diminish the resistance. Cells of this kind have been kept joined up through a resistance of 20 or 30 ohms for weeks together without any perceptible diminution in the E.M.F. The alkaline solution must not be too dilute or the zinc will soon become coated with oxide.

The author states that his zinc-bromine-platinum cell is still better for giving a continuous current through a high resistance. It requires no porous cell, has a high E.M.F., and has been kept in continuous action for months without any change in the E.M.F., in fact until one or other of the elements was completely decomposed. The only precaution necessary is to cover the bromine with a layer of petroleum, which completely prevents all evaporation and smell.

G. W. T.

Electrolytic Formation of Hydrogen Peroxide at the Anode.
By M. TRAUBE (*Ber.*, 20, 3345—3351).—From the results of previous

experiments (Abstr., 1885, 1108), it was concluded that hydrogen peroxide is formed by the union of molecular oxygen with hydrogen. Richarz, on the other hand (this vol., p. 11), maintains that that hydrogen peroxide is produced by the oxidation of water.

When 1 per cent. sulphuric acid is electrolysed in presence of alcohol or hydrogen peroxide at the anode, these are rapidly oxidised. In the electrolysis of a 1 per cent. solution of chrome alum, not a trace of ozone is formed, and chromic acid appears at the anode. When lead is used as anode in the electrolysis of 1 per cent. sulphuric acid, it becomes covered with lead peroxide. These experiments point to the presence of free oxygen-atoms which only unite to passive molecules when there is nothing to oxidise, and also show that water is not oxidised by oxygen-atoms. In the electrolysis of sulphuric acid, it is suggested that persulphuric acid is formed by the action of nascent oxygen, and that this decomposes into sulphuric acid (2 mols.) and hydrogen peroxide (1 mol.).

As further proof in favour of the constitution previously ascribed to hydrogen peroxide (Abstr., 1886, 660), it is mentioned that the peroxides of hydrogen, of the alkalis and alkaline earths, of zinc, cadmium, and copper, have quite different chemical properties from those of lead, silver, manganese, and nickel, &c. Only those of the first group yield hydrogen peroxide when treated with acids. The peroxides of the second group can all be prepared by oxidising the oxides or hydroxides in alkaline solution. The peroxides of the first group possess powerful reducing properties, whilst those of the second group are indifferent to oxidising agents. Hence it is concluded that the peroxides of the two groups are differently constituted, and that hydrogen peroxides cannot have the formula $\text{HO}\cdot\text{OH}$. The constitution represented by the formula $\text{H}\cdot\text{O}:\text{O}\cdot\text{H}$ is considered to be the only one possible.

N. H. M.

Electrolytic Conductivity of Halogen-compounds. By W. HAMPE (*Chem. Zeit.*, 11, 816; 846—847; 904—905; 934—935; 1109—1110; 1158).—Pure dry salts fused in hard glass tubes or porcelain crucibles, or dissolved in dry ether or absolute alcohol, were submitted to a current from eight large Bunsen chromic acid cells, platinum electrodes being used when the conditions of experiment permitted. The following salts proved good electrolytes in a state of fusion:—All the haloid salts of lithium, sodium, potassium, rubidium, and caesium, beryllium chloride, magnesium chloride and bromide, strontium and calcium chlorides and bromides (part of the liberated metals combining with the silica of the glass or porcelain), barium chloride, lanthanum, didymium, and cerium chlorides (this confirms Hillebrand and Norton's experience), indium chloride, thallous and cuprous chlorides (thallic and cupric chlorides decompose when fused), tantalum chloride, and thorium chloride, although the latter is not suitable for electrolysis, as the melting and boiling points are near together. In concentrated alcoholic solutions, cupric chloride behaves as an electrolyte. Gold chloride in carbon bisulphide is a non-conductor; when mixed with ether a pasty mass forms, and the supernatant

liquid gradually deposits gold; this liquid conducts slightly, and after 15 minutes the negative pole becomes gilded. Aqueous solutions of gold chloride owe their electrolytic conductivity to the presence of hydrochloric acid. Zinc and cadmium iodides, bromides, and chlorides are good electrolytes when fused, but their conductivity ceases on solidification. In concentrated solutions, these salts conduct well, in weak solutions badly; in absolute alcohol all, but only zinc chloride and bromide dissolve in ether and conduct well, whilst the other salts dissolve in ether and conduct only sparingly or not at all. Fused mercuric chloride, bromide, and iodide are feeble electrolytes, especially the first; in solution in ether, none conduct, owing probably to sparing solubility; in absolute alcohol, they conduct slightly; better when the solution is hot than when it is cold. Mercurous chloride fused in closed glass vessels proved electrolytic. Aqueous solutions of mercuric chloride conduct badly at first, with deposition of mercury and mercurous chloride, and evolution of oxygen and chlorine; subsequently mercury only is deposited, and the electrolysis proceeds at a quicker rate; in this case the current in the first instance produces electrolytes (hydrochloric acid for instance), and when these are present in abundance the process goes well.

Fused gallous chloride is a very good conductor, globules of metal separate at the negative pole, but the chlorine at the positive pole combines with the gallous chloride to form gallic chloride; the latter is not such a good conductor as gallous chloride, no metal separates, evidently owing to its entering into combination with the gallic chloride to form gallous chloride. Stannic chloride does not conduct; when electrolysed in aqueous solution the hydrochloric acid only conducts, the tin being set free by the hydrogen (Hittorf has stated the contrary). Fused stannous chloride on the other hand is an excellent electrolytic conductor, the current continues to pass even on cooling as long as the mass remains soft, but ceases to flow when the chloride is solid. Fused lead chloride, bromide, and iodide conduct very well with vigorous decomposition, and, unlike the other salts examined, ~~they conduct when solid~~; Buff characterised this conduction as metallic, Wiedermann regarded it as electrolytic; the author confirms the latter view. At ordinary temperatures, no current passes through the cold fused lead salts; it is first observed to flow at 110° through the chloride, at 115° through the bromide, and at 150° through the iodide, the conductivity then increases as the temperature rises, in the manner usual with electrolytes. The trihaloid compounds of antimony in a fused state behave as feeble electrolytes, the tri-iodide being the best; but in carbon bisulphide solutions they do not conduct electricity. Vanadium tetra- and tri-chlorides do not conduct, but when decomposed with water the solutions electrolyse, but in neither case is the metal deposited. The following are non-conductors:—Fused aluminium chloride or bromide (Buff's statement to the contrary is probably based on experiments with impure chloride), boron chloride, titanium and silicon tetrachlorides and bromides, vanadyl chloride, niobium pentachloride, all the haloid compounds of phosphorus, arsenic trichloride, and antimony pentachloride. Yttrium and zirconium chlorides sublime without melting, and when

the former is dissolved in water it conducts on account of the hydrochloric acid, but no metal is deposited; the latter is a non-conductor; titanium hexa- and di-chlorides are infusible solids, so do not come under consideration.

D. A. L.

Molecular Heats of Gases. By H. LE CHATELIER (*Bull. Soc. Chim.*, **48**, 122—124).—The fact that the curves of the specific heats of carbonic anhydride and water vapour converge to a point below zero, leads to the supposition that molecular heats of all gases tend to the same limit as the temperature approaches absolute zero. The author has compared the specific heats, calculated on this assumption, with the actual determinations of Wiedemann. The specific heats can be represented by the expression $C = 6.8 + \alpha[273 + t]$, α being a constant which depends on the nature of the gas and has a higher value the more complex the molecule. The numbers calculated by this equation differ from the actual numbers by quantities less than the experimental errors. A similar agreement is found between the numbers for carbonic anhydride at high temperatures deduced from this equation and the actual numbers obtained by the author and Mallard.

C. H. B.

Influence of Small Amounts of Impurities on the Vapour-tension of Liquids. By G. TAMMAN (*Ann. Phys. Chem.* [2], **32**, 683—699).—The increase in the vapour-tension of a liquid observed by Wüllner and Grotian (*Ann. Phys. Chem.* [2], **11**, 545), when the space occupied by its vapour in the manometer has been decreased by compression, and attributed by them to a dependence of the tension on the amount of liquid in contact with the vapour, is shown to be caused and brought about by traces of impurity in the liquid. These traces are often so exceedingly small as not to be recognisable by the ordinary tests. But the vapour, if containing this impurity, consists of a mixture of two substances one of which is more volatile than the other, so that compression causing a greater condensation of the less volatile, causes a rise in the vapour-tension, and expansion has just the opposite effect. A difference is therefore observed between the tension measured after compression and after expansion. This difference is reduced in magnitude by purification of the liquid used, but could not in any case be entirely eliminated, although an approximation to a constant tension was reached in the case of water. A measurement of the vapour-tension, once after compression and once after expansion, will give a rough measure of the purity of the substance used. Experiments are given with water, ether, carbon bisulphide, benzene, methyl and ethyl alcohols, chloroform and acetic acid.

H. C.

Dissociation of Crystallised Lead Acetate and Sodium Thiosulphate. By W. MÜLLER-ERZBACH (*Ber.*, **20**, 2974—2981).—Two series of experiments were made with lead acetate. In the first series, large crystals of the commercial salt were employed in the state of powder, and with it the relative tension was 0.27 to 0.38 at temperatures varying between 12.5° and 21.8°; whilst in the second series, in which

small crystals of the pure salt were used, the relative tension was 0.32 to 0.39 at 14.9—24.3°; the value of $t_1 - t_2$, which the author assumes to be a measure of the attraction between the salt and its water of crystallisation (compare Abstr., 1887, 628), decreasing with the rise of temperature. A partially dehydrated specimen of the salt containing about $\frac{1}{2}$ mol. H_2O , when placed in a moist atmosphere until water equal in amount to 3 mols. had been absorbed, showed a higher and less constant relative tension, the highest value being 0.485 at 21.5°.

With sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O}$, two series of experiments were also made, and in the first series 3 mols. H_2O were lost with a relative tension = 0.33 to 0.36 at 29.1—32.9°, and a further 1.4 mol. with a relative tension = 0.17 to 0.22 at 31.7—34.2°, the remainder of the water being given off with a relative tension = 0.047 to 0.053 at 50.6—52.7°. The second series of experiments showed that 3 mols. were lost with a relative tension = 0.26 to 0.28 at 18.3—21.6°, that a further 1.4 mol. was lost with a relative tension = 0.08 to 0.12 at 15.9—22.1°, and that the tension became imperceptible when the salt contained 0.6 mol. H_2O . The partially dehydrated salt, containing 2 mols. H_2O , exposed in a moist atmosphere until it contained 4.75 mols. H_2O , lost 2.55 mols. with a relative tension = 0.29 to 0.31 at 23.6—25.9°, and the salt with 2 mols. H_2O , obtained in like manner from the salt + 0.49 mol. H_2O , lost approximately 1.5 mol. with a relative tension = 0.10 to 0.19 at 5.3—16.1°. It was found, however, that when sodium thiosulphate was heated to drive off the water of crystallisation rapidly and then exposed to moist air until 4.9 mols. H_2O had been taken up, it lost the whole of the water with a relative tension = 0.21 to 0.32 at 15.8—30.6. W. P. W.

Relation between the Compressibility of a Solution and the Compressibilities of its Constituent Parts. By F. BRAUN (*Ann. Phys. Chem.* [2], **32**, 504—508).—Röntgen and Schneider (this vol., p. 22) have given for the compressibility of rock-salt the value 5×10^{-6} , which does not agree with the author's previous determination (Abstr., 1887, 436), which gave 1.4×10^{-6} . This result was obtained by comparatively rough methods, but the author points out that it agrees very closely with the value 1.6×10^{-6} , deduced from Voigt's determination (*Ann. Phys. Chem. Ergbd.*, **7**, 214) of its two coefficients of elasticity.

Röntgen and Schneider assume that if γ be the compressibility of a solution containing per unit volume a volume V' of water, and V'' of salt, and if γ' be the compressibility of water and γ'' that of the salt, then (1) $\gamma = \gamma'V' + \gamma''V''$. Now if n be the number of molecules in a solution containing a percentage p of salt of molecular weight m , then (2) $n = 10^6 p / m(100 - p)$. They then take a constant a such that (3) $n = aV''/V'$, and eliminating V' and V'' from equations (1) and (3), they obtain the equation $(\gamma - \gamma')(n + a) = (\gamma' - \gamma'')a$, which they write $(y - b)(n + a) = (1 - b)a$, where y is the apparent compressibility of the solution, and b that of the salt. If κ be the cubic compressibility of glass, (5) $y = (\gamma - \kappa)/(\gamma' - \kappa)$, and

$b = (\gamma'' - \kappa)/(\gamma - \kappa)$. They determined n and y for five different concentrated solutions of sodium chloride. Two of these results they used to determine a and b by means of (4). They then found that by substitution in (4) the relations obtained between n and y agreed well with the experimental determinations. Assuming the formula to hold good when n becomes infinite, y will in that case be equal to b , and determining γ'' from (5), they obtained values varying from 4.7×10^{-6} to 4.8×10^{-6} , which agreed well with the value 5×10^{-6} determined directly for the solid salt.

In a previous memoir, the author found that (1) does not agree with experiment, if for example γ' were given, γ'' would have to be negative to give the correct value of γ . If, therefore, the compressibility of a solution is equal to the sum of the compressibilities of its constituents, the compressibility of the water of the solution must be diminished by the presence of the salt, and this is shown to be the case by Röntgen and Schneider's recent results. The other discrepancy the author traces to these observers having determined the value of a from two equations of the form (4), the observations then show that a and b are constants, so that if the value of V'' calculated from (3) be substituted in (1), this equation will naturally agree with experiment, since it is merely another form of (4). The value of a can, however, be obtained directly from (2) and (3), and the value thus obtained is about five times as great as before, and (1) will only hold good for this value of a , for then only does the ratio V''/V' express the actual conditions. With this value of a , b is no longer found to be a constant. The author gives a numerical example, in which Röntgen and Schneider's value of a leads to an impossible result. He observes that as this correction does not alter the form of (4), all conclusions drawn simply from the form of this equation will still hold good.

G. W. T.

Dilatation and Compressibility of Liquids. By E. H. AMAGAT (*Compt. rend.*, 105, 1120—1122).—The author has determined the expansion and compressibility between 0° and 50° , and 1 atmosphere and 3000 atmospheres, of water, of ether, of methyl, ethyl, propyl and allyl alcohols, of ethyl chloride, bromide and iodide, of carbon bisulphide and of phosphorous chloride.

In all cases, except that of water, the coefficient of expansion diminishes with increased pressure, but the rate of diminution decreases as the pressure rises, although it remains distinct even at 3000 atmospheres. The increase in the coefficient of expansion due to a rise of temperature, likewise diminishes under increased pressure. The coefficient of expansion of ether under a pressure of 3000 atmospheres is only one-third of its value at normal pressure, and when this liquid is compared with carbon bisulphide, it is found that whilst under normal pressure the ether is much the more expansible of the two, under 2500 atmospheres the coefficients are identical, and under 3000 atmospheres the coefficient for carbon bisulphide is higher than that for ether.

Under very high pressures, the perturbations which are observed in the case of water, and which are due to the existence of a point of maximum density, gradually disappear, and under 3000 atmospheres

the law of expansion of water agrees with that of other liquids (compare Abstr., 1887, 695).
C. H. B.

Compressibility of an Aqueous Solution of Ethylamine. By F. ISAMBERT (*Compt. rend.*, **105**, 1173—1175).—The coefficient of compressibility of ethylamine between 5° and 7° and from 8 to 45 atmos. is 0·000120, a value which approximates to that for ether at 0°, and is much higher than that for water. The compressibility of an aqueous solution of ethylamine is much lower than the value calculated on the assumption that the two liquids are simply mixed, and it decreases as the proportion of water increases. Ethylamine in fact behaves like ammonia, and this result confirms the author's conclusion that solutions of the ammoniacal bases behave like true chemical compounds more or less dissociated in presence of excess of water. The view that a compound is formed is supported by the contraction which takes place, and the development of heat, which as in the case of ammonia is equal to the heat of volatilisation of the amine.

C. H. B.

Oxygen Carriers. By L. MEYER (*Ber.*, **20**, 3058—3061).—Experiments were made with various metallic salts with a view to determine their power of expediting the oxidation of sulphurous acid. The oxygen and sulphurous acid were passed, for four hours, at as uniform a rate as possible, through the solution of known concentration contained in a flask heated on a water-bath. The amount of sulphuric acid was then determined.

The most active salt was manganous sulphate, of which 2·404 grams ($\text{MnSO}_4 + 5\text{H}_2\text{O}$) was dissolved in 200 c.c. of water; this solution in four hours gave six times as much sulphuric acid as the salt contained. Manganous chloride is also very active; copper sulphate gives less sulphuric acid. After copper salts, the salts of iron and cobalt are the most active, the chlorides being more so than the sulphates. The salts of nickel, zinc, cadmium, and magnesium produce less sulphuric acid, whilst dilute solutions of thallium and potassium sulphates and free sulphuric acid produce none at all (compare Kessler, *Ann. Phys. Chem.*, 1863, 119, 218).

N. H. M.

Explosive Decomposition of Picric Acid and other Nitro-derivatives. By BERTHELOT (*Compt. rend.*, **105**, 1159—1162).—When picric acid is heated in a capsule, it melts and gives off inflammable vapours, which burn with a smoky flame, but it does not explode. A small quantity when heated in a closed tube can be sublimed without decomposition. If, however, the picric acid is thrown into a vessel previously strongly heated, the quantity of the solid being so small that the temperature is not materially reduced, then it decomposes with detonation accompanied by a vivid flash of light. When the quantity of picric acid introduced is sufficient to somewhat cool the bottom of the vessel, detonation does not take place at once, but the acid is partially volatilised, and a somewhat less violent explosion follows. If the quantity is still larger, the acid decomposes, but there is no explosion. Similar results were obtained with mono- and di-

nitrobenzene, and mono-, di-, and tri-nitronaphthalene. The tendency to detonate increases with the number of NO_2 groups.

Nitro-derivatives may decompose in several different ways. If the heat developed by combustion is carried away with sufficient rapidity, there is no deflagration or detonation, but if the heat accumulates the temperature may rise sufficiently high to produce detonation. The heating of only a small part of the containing vessel to a high temperature may produce an explosive wave, which may then propagate itself through the whole mass, and thus produce an explosion.

C. H. B.

Relative Size of the Molecules, calculated from the Electric Conductivity of Salt Solutions. By G. JÄGER (*Monatsh.*, 8, 498—507).—In this paper, an attempt is made to determine the relative diameters of some of the elementary molecules and atomic groupings, adopting as a basis for the calculations the results obtained by Kohlrausch in his investigations on the electric conductivity in aqueous solutions of certain metallic hydroxides and salts.

If, in such an aqueous solution, a cylindrical section is taken of unit dimensions, there are contained therein m electrochemical molecules; taking, then, the electromotive force in the direction of the axis as unity, the kation will be propelled in the one direction with velocity U , and the anion with velocity V in the other. If ϵ is the quantity of positive or negative electricity with which each molecule is endowed, then the coefficient of conductivity $\kappa = (u + v)m$ where $\epsilon U = u$ and $\epsilon V = v$, and the specific molecular conductivity $\lambda = u + v$. But according to Hittorf $v/u + v = n$, in which n is the number of molecules passing in unit time through unit space. Hence $u = (1 - n)\lambda$ and $v = n\lambda$. If the molecules of the ions pass with a certain velocity, they meet in unit time a certain number of other molecules of a different kind passing in the opposite direction; therefore they require a certain amount of energy to overcome the necessary resistance which is proportional to their rate of passage. If for the sake of simplicity the molecules are assumed to be spheres, and the solution is so dilute that there is no interaction between the molecules of the dissolved substance; also if a molecule of radius r passes in a certain direction whilst the environment consists of molecules of radius ρ , and the number of molecules in unit volume is α , then $r + \rho = R$ if the forces are resolved in two directions. The result is the same if the radius of the moving molecule is R , whilst the molecules in the environment are reduced to a mathematical point.

Now (1) $v = C/R^2 = C/(r + \rho)^2$, in which C is a constant obtained by integration, while for another molecule (2) $v' = C/(r' + \rho)^2$; dividing (1) by (2) $v/v' = (r' + \rho)^2/(r + \rho)^2$, from which $r = (r' + \rho)\sqrt{v'/v} - \rho$. To solve this equation the values for the relative velocities have been determined by Kohlrausch, whilst to find r' and ρ the diameters of the molecules of water and chlorine calculated by O. Meyer are used. The values are for water $d = 96 \times 10^{-9}$, for chlorine $\delta = 44 \times 10^{-9}$ centimetres, while U for water = 49. Hence the diameter of a given molecule is—

$$d = \sqrt{\frac{960,400}{v}} - 44$$

expressed in 10^{-9} centimetres. The following results are given for the relative diameters of the elementary molecules and of certain atomic groupings arranged in order of magnitude.

H.	$\frac{1}{2}\text{H}_2$.	I.	Br.	(CN).	Cl.	K.	(NH ₄).	(NO ₃).	(ClO ₃).
15	32	91	91	95	96	97	99	100	111
$\frac{1}{2}\text{K}_2$.	$\frac{1}{2}(\text{SO}_4)$.	Ag.	$\frac{1}{2}(\text{NH}_4)_2$.	$\frac{1}{2}(\text{CO}_3)$.	$\frac{1}{2}\text{Ag}_2$.	Na.	F.	$\frac{1}{2}\text{Ba}$.	
111	111	111	117	119	129	132	135	138	
$\frac{1}{2}\text{Cu}$.	$\frac{1}{2}\text{Sr}$.	$\frac{1}{2}\text{Ca}$.	$\frac{1}{2}\text{Mg}$.	(C ₂ H ₃ O ₂).	$\frac{1}{2}\text{Na}_2$.	$\frac{1}{2}\text{SO}_4$.*	Li.	$\frac{1}{2}\text{Zn}$.	
138	141	148	160	160	165	165	170	175	
			$\frac{1}{2}\text{Mg}$.*	$\frac{1}{2}\text{Zn}$.*	$\frac{1}{2}\text{Cu}$.*	$\frac{1}{2}\text{Li}$.*			
			218	239	239	251			

The values marked thus * were determined by the electric conductivity of magnesium, copper, and zinc sulphate.

It will be seen that the relative size of the molecules is most variable, that of lithium, for example, being more than 16 times greater than that of hydrogen, both being expressed in linear dimensions. It is further to be noticed that the diameters of the double molecules of the elements, as for instance hydrogen, is greater than that of twice the single molecule, but this result would be a necessary consequence of the union of two spheres of equal volume.

The elements belonging to the same family in Mendeléeff's scheme, such as chlorine, bromine, iodine, or barium, strontium, and calcium, come close together in the table. If a substance is in the solid or liquid state, the number of molecules in unit volume is directly proportional to the volume of the molecule; multiplying this number by the molecular weight, values should be obtained proportional to the specific gravities of the elements in question, or conversely similar proportional numbers should be obtained by dividing the molecular weight by the molecular volume. However, this relation does not always hold good, except in the case of certain chemically allied elements. Hence it follows that different molecules consist of ultimate particles differently arranged.

V. H. V.

Representation of Atoms in Space. By W. LOSSEN (*Ber.*, 20, 3306—3310).—If atoms be considered as material points, the tetrahedron employed in the Van't Hoff-Le Bel hypothesis to represent the compound C(R₁R₂R₃R₄) may be replaced by the straight lines joining the points at the solid angles where the radicles are assumed to be situated with a point in the centre representing the carbon-atom. The attractive forces by which the radicles R₁R₂R₃R₄ are held by the carbon-atom must then act in the directions of these straight lines, the said directions being solely dependent on the positions of the atoms in space. A combination of two carbon-atoms is then

effected by an attraction acting along and represented by the straight line joining them. By such a representation, however, a double union would be in no way distinguishable from a single one, both being denoted by a straight line joining the carbon-atoms. The author considers this to indicate a weak point in the Van't Hoff - Le Bel hypothesis, and one requiring explanation. He also concludes that a polyvalent atom cannot be represented as a point in space, but that various portions of such an atom having different affinities must be distinguished.

H. C.

Inorganic Chemistry.

Preparation of Hydrogen Iodide. By L. MEYER (*Ber.*, 20, 3381—3383).—100 parts of iodine contained in a retort are moistened with about 10 parts of water. The retort is then fitted with a funnel closed with a glass rod, containing 5 parts of amorphous phosphorus mixed with 10 parts of water. One drop of water containing phosphorus is let into the retort; more phosphorus is slowly added, after which large amounts may be added. The mixing is completed in a quarter of an hour. If more than a drop is added at first, the action cannot be controlled, and will generally result in a violent explosion. No heating is necessary. The iodine carried over by the hydrogen iodide is nearly all deposited in the neck of the retort, which is inclined upwards.

By using 100 grams of iodine, 5 grams of phosphorus, and 25 c.c. of water, 95 grams of hydrogen iodide (of which 37.5 grams were obtained by distillation) were obtained, instead of 100.8 grams. With 20 grams of water 98.1 grams were obtained (74.4 grams as gas and 23.7 grams by distillation).
N. H. M.

Products and Rate of Decomposition of the Salts of the Halogen Oxy-acids by Heat. By A. POTILITZIN (*Chem. Centr.*, 1887, 1218, from *J. Russ. Chem. Soc.*, 1887, 339—357).—Between 330° and 400°, barium chlorate decomposes entirely according to the equation $2\text{Ba}(\text{ClO}_3)_2 = \text{BaCl}_2 + \text{Ba}(\text{ClO}_4)_2 + 4\text{O}$. Between 400° and 470°, barium chloride and oxygen are the only products. The rate of the decomposition rises with the temperature up to 400°, whilst if the temperature remains constant, the decomposition rises at first, and then gradually falls again, although it is not complete. According to the author, barium chlorate decomposes to some extent before it melts. Barium perchlorate crystallises with 3 mols. H_2O , whereas Marignac gives the formula $\text{Ba}(\text{ClO}_4)_2 + 4\text{H}_2\text{O}$; also, contrary to Marignac's statement, it is not hygroscopic. It loses 2 mols. H_2O by remaining over sulphuric acid, and the third molecule is expelled at 100°.

Barium bromate becomes anhydrous at 170°, the crystals turning

slightly yellow, without, however, losing their crystalline form or lustre. Decomposition begins at 260° , and at 300° bromine is evolved. The decomposition becomes complete without the salt melting. The author draws the conclusion that the bromate is changed into two isomeric salts, namely $\text{BrVO}_3 \cdot \text{OM}$ (the original salt), and $\text{MBr}^{\text{VI}}\text{O}_3$, and that these, therefore, decompose at different rates. He could not find any perbromate in the product of decomposition. J. W. L.

Mutual Displacement of the Halogens in their Compounds with Oxygen. By A. POTILITZIN (*Chem. Centr.*, 1887, 1218—1219; from *J. Russ. Chem. Soc.*, 1887, 358—364).—The author believes that these reactions are much more complex than is usually supposed. By the action of chlorine on a solution of sodium bromate in the dark, he obtained a mixture of sodium chloride and bromide, and bromic and chloric acids together with free bromine. He finds that chlorine acts in the same way on potassium bromate and on barium bromate; experiments were also made on the dry salts, when the same products seemed to be formed. Bromine was also found to act on the chlorates in the same way, although much less energetically. These reactions take place much more readily in a sealed tube. Iodine and the iodates were also included in the series of experiments with similar results. J. W. L.

Preparation of Hydrogen Sulphide Free from Arsenic. By C. WINKLER (*Zeit. anal. Chem.*, 27, 26—27).—Barium sulphate (powdered barytes) is mixed with 25 per cent. of ground coal and 20 per cent. of common salt. The damped mixture is rammed into a clay crucible, which after drying and closing with a luted cover is heated for several hours at an incipient white heat. The product is in hard compact masses which dissolve completely in dilute hydrochloric acid with a steady evolution of hydrogen sulphide.

M. J. S.

Selenites. By BOULZOUREANO (*Bull. Soc. Chim.*, 48, 209—210).—Solutions of metallic salts were mixed with sodium selenite and the resulting precipitates were heated in sealed tubes at 200° with very dilute selenious acid. Ferric selenite forms small, golden-yellow prisms which separate in radiating groups.

Another method consists in treating a metallic carbonate with dilute selenious acid, mixing the solution with its own volume of water, and heating in sealed tubes at 200° . This was employed for the preparation of the cobalt, nickel, manganese, and cadmium salts.

Cobalt selenite forms transparent, violet prisms, nickel selenite forms large, short, green prisms arranged in radiating groups. If the original solution is mixed with sodium selenite, yellow crystals are obtained. Manganese selenite crystallises in short, pale-red prisms or in slender, brown needles if heated beyond 230° . The cadmium salt forms long, colourless, transparent prisms, or much shorter yellow crystals if heated at about 200° . Zinc seems to form a selenite crystallising in prisms.

The liquid obtained by the second method was allowed to evaporate spontaneously at the ordinary temperature or in a vacuum. Crystals

are obtained in the case of cobalt and manganese. The latter yields a pink-coloured crust and the former deep violet crystals.

Cupric carbonate, when treated with a warm solution of selenious acid, yields a blue precipitate of the normal selenite, and if this is heated to boiling, it is converted into green, microscopic prisms. The solution is bluish-green, and on cooling deposits large, green crystals. If the normal selenite is heated in sealed tubes with the carbonate and water, it yields well-defined, greenish-yellow, prismatic crystals. Sodium selenite and zinc sulphate in sealed tubes yield white, transparent crystals.

C. H. B.

Preparation of Hydrogen Arsenide. By A. CAVAZZI (*Chem. Centr.*, 1887, 1097, from *Rend. Acc. Bologna*, 1886-87, 85-86).—The action of zinc on an acid solution of arsenious acid produces a gas containing 70 per cent. by volume of hydrogen arsenide. Sodium amalgam containing not more than 4 grams of sodium in 50 c.c. of mercury, by its action on a concentrated solution of arsenious acid, produces a gas containing 86 per cent. by volume of hydrogen arsenide. A gas containing a large quantity of arsenic may be prepared by the action of aluminium on a somewhat dilute alkaline solution of potassium arsenite, whilst a solution of arsenic disulphide in potash, when subjected to the action of aluminium, evolves a gas quite free from arsenic.

J. W. L.

Action of Hydrogen Arsenide on Arsenious Acid. By D. TIVOLI (*Chem. Centr.*, 1887, 1097, from *Rend. Acc. Bologna*, 1886-87, 98).—The reactions of hydrogen arsenide on arsenious acid dissolved in hydrochloric and sulphuric acid respectively are expressed by the equations:— $2\text{AsH}_3 + 2\text{AsCl}_3 = 6\text{HCl} + \text{As}_4$ and $3(\text{AsO}_2)\text{SO}_4 + \text{H}_2\text{SO}_4 + 6\text{AsH}_3 = 3\text{As}_4 + 4\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O}$. The precipitation of the arsenic does not take place in neutral solutions, whereas in the hydrochloric acid solution it is complete, and in the sulphuric acid solution almost so.

J. W. L.

Lowest Compounds of Silver. By O. v. D. PFORDTEN (*Ber.*, 20, 3375-3381; compare *Abstr.*, 1887, 699).—According to Stas, silver is oxidised in the cold in presence of water containing dissolved air and acidified with hydrochloric, sulphuric, or acetic acid, &c. Experiments made by the author show that when a solution containing potassium permanganate and sulphuric acid is boiled in a current of carbonic anhydride it is not capable of dissolving finely divided silver; on admitting air to the solution, silver dissolves and the permanganate becomes decolorised. This accounts for the result previously obtained (*loc. cit.*) when silver was boiled with dilute sulphuric acid and treated with a drop of permanganate solution; the solution being free from air, the permanganate did not decolorise. In presence of air, the reaction is very slow, and in the titration of the argentous oxide with permanganate, none of the silver formed is dissolved (compare Friedheim, *Abstr.*, 1887, 1079).

With regard to Friedheim's supposition (*loc. cit.*) that the argentous oxide is a mixture of silver and argentic oxide or organic matter, it is

mentioned that the preparation previously described contained no carbon and dissolved in nitric acid without leaving a residue; when shaken for 12 hours with mercury, it underwent no change in properties or appearance. It is therefore maintained that the substance cannot be metallic silver. The examination of the substance will be continued.

N. H. M.

Behaviour of Basic Slag with Water charged with Carbonic Anhydride. By M. A. v. REIS (*Chem. Zeit.*, **11**, 933—934; 981—982).—In these experiments, which are a continuation of those previously made by him (*Abstr.*, 1886, 663), the author has included nine samples of slag from different sources; two samples of precipitated slag; one sample each of di-, tri-, and tetra-calcium phosphate (the last synthetically prepared), also bones, bone-ash, and phosphorite. Ten grams of the finely powdered phosphate supported on a platinum cone covered with asbestos in a funnel, were treated with water saturated with carbonic anhydride percolating at the rate of 1 litre in three hours. One slag was treated with 50 litres of carbonic anhydride solution; each litre of the first 10 litres of percolate was examined separately, but subsequently examinations were made at definite intervals. Silica and phosphoric acid pass through in nearly constant quantities in proportions approximating to their relative amounts in the original slag up to the 25th litre, after which their solubility rapidly decreases; lime, however, continues to dissolve even in the 50th litre. Although the various changes take place simultaneously at first, the free lime is most readily attacked, then the calcium silicate and phosphate, and finally the other compounds of calcium (probably ferrite or manganate). The exhausted slag amounted to 30·07 of the original; its composition (I), and that of the original slag (II), is as follows:—

	SiO ₂ .	P ₂ O ₅ .	CaO.	MgO.	MnO.	FeO.	Fe ₂ O ₃ .
I.	2·30	2·25	14·7	6·65	9·09	18·41	35·90
II.	7·67	16·32	47·98	2·47	4·18	8·90	7·41

	Al ₂ O ₃ .	Insoluble.	Loss on ignition.
I.	5·52	2·25	3·10
II.	—	0·47	—

The slight solubility of the magnesia is noteworthy. The other phosphates and slags were treated each with 10 litres of carbonic anhydride water, and the percolates were examined in two lots of 5 litres each. Full numerical details are given, from which the following table is taken, showing the relative solubility of the phosphoric acid, silica, and lime in the various phosphates examined; the figures are percentages of the amount of each constituent in the original substances:—

	SiO ₂ .	P ₂ O ₅ .	CaO.
Slags	86.1—27.4	48.1—22.9	57.5—34.4
Tetracalcium phosphate	—	42.1	53.0
Bones	—	28.5	28.9
Precipitated slags	7.7—22.7	22.0—33.0	30.1—58.5
Dicalcium phosphate..	—	16.8	16.8
Tricalcium „ ..	—	12.5	13.6
Bone ash.....	—	5.5	5.9
Phosphorite	—	3.1	3.8

The slags varied considerably amongst themselves owing to their different origin and constitution, but along with the tetracalcium phosphate they proved more soluble than the other forms of phosphate; the comparatively high solubility of bone phosphoric acid is due to the organic matter present. It is interesting to note that in experiments with the tetracalcium phosphate after the removal of any excess of lime in the first 5 litres or so, the phosphoric acid and lime wash out in the molecule ratio $1\text{P}_2\text{O}_5 : 4\text{CaO}$, tending to show that this really is a compound of that composition, for had it been a mixture of lime and triphosphate, the lime would have continued to wash out irregularly. In a similar manner, the existence of tetracalcium phosphate in basic slag is illustrated.

The author concludes that he has now set aside v. Maltzahn's adverse criticism of his previous work, and upset any views as to the comparative insolubility of basic slag phosphates. D. A. L.

Tetrabasic Calcium Phosphate and the Basicity of the Silicate in Basic Cinder. By G. HILGENSTOCK (*Chem. Centr.*, 1887, 1097—1098, from *Stahl u. Eisen*, 7, 557—560).—The author has succeeded in preparing tetrabasic calcium phosphate by fusing together calcium phosphate or phosphoric acid with lime, using fluorspar as a flux. The author points out further that since calcium triphosphate is reduced by metallic iron when fused, it can only be the tetrabasic phosphate which is contained in the basic slag, and that the difference in crystalline form of this phosphate may be accounted for in somewhat the same way as in the formation of the various modifications of antimonious oxide, valentinite and senarmontite. Observations seem to show that as the flux cools, the rhombic plates are first formed, next the hexagonal needles, and finally the monosymmetrical crystals. In conclusion, the author endeavours to prove that the silica can only be present in the form CaSiO_3 . J. W. L.

Behaviour with the usual Solvents of the Soluble Phosphoric Acid in Superphosphates, which have remained some time in Bulk. By A. BEYER (*Chem. Centr.*, 1887, 1115, from *Rep. anal. Chem.*, 7, 327—330).—In making a series of determinations to compare Petermann's and Wagner's methods for the estimation of the phosphoric acid soluble in ammonium citrate, the author found that not only was the percentage of phosphoric acid soluble in water reduced by long standing in heaps, but also that soluble in ammonium citrate solution as estimated by Wagner's method. The alteration in the percentage

of phosphoric acid as estimated by Petermann's method, was less noticeable. In superphosphates containing but little ferric oxide and alumina, the differences between the results obtained by the two methods were not very great, but even at the end of eight days an appreciable loss of soluble phosphoric acid as determined by Wagner's method was observed, which quantity was not so great where considerable quantities of acid had been employed. Petermann's method does not show so great a change in the soluble character of the phosphoric acid in superphosphates after a time. If the superphosphates contain considerable quantities of ferric oxide and alumina, the results as obtained by the two methods vary almost directly after manufacture, which differences increase the longer the superphosphates are kept. Here also the results obtained with Petermann's method remain almost constant, whilst the percentage as determined by Wagner's method, as also the phosphoric acid soluble in water, decreases.

J. W. L.

Cadmium Sulphide and the various Cadmium Pigments of Commerce. By G. BUCHNER (*Chem. Zeit.*, **11**, 1087—1089; 1107—1109).—The author finds that all the forms of cadmium sulphide have the same percentage composition represented by the formula CdS , but that two modifications exist, one lemon-yellow, the simple CdS , the other a polymeride of it, and of a vermilion colour. The variety of colour in different preparations of cadmium sulphide is due to the mixture of these two modifications in varying proportions, and not to the small quantity of soluble cadmium salt retained by the sulphide during its precipitation, as has been suggested. The yellow variety is readily polymerised into the red variety by dilute acids, alkalis, &c., especially when in the nascent state, hence on precipitating solutions of cadmium salts with hydrogen sulphide, at first the yellow sulphide forms, but, as the liberated acid comes into action, the red sulphide is precipitated, and if the solution is acid beforehand, little or no yellow sulphide is produced. The red variety passes through the yellow stage when dissolved in acids. Sodium sulphide produces the yellow sulphide in dilute solutions of a cadmium salt, a reddish precipitate in strong solutions, and a brick-red one in boiling solutions. Polysulphides of potassium or ammonium precipitate the yellow cadmium sulphide mixed with varying quantities of finely divided sulphur, which can be extracted by carbon bisulphide. It is noteworthy that pure (red or yellow) cadmium sulphide is quite stable in light, whereas this mixture of sulphide and sulphur oxidises rapidly in light (not in darkness), becoming dirty white, especially after it is ground with linseed oil.

Cadmium hydroxide also assumes two forms: the simple one prepared by adding sodium hydroxide to solutions of cadmium salts gives rise to the yellow sulphide with sodium sulphide, &c.; the polymeric one is formed when cadmium solutions are poured into solutions of sodium hydroxide or when they are precipitated hot; this hydroxide produces the red sulphide, with an intermediate dicadmium sulphhydroxide, $\text{Cd}_2\text{S}(\text{OH})_2$, of a fine red colour, but too unstable for a pigment; the author considers this association of red colour with the two cadmium atoms in a single molecule, supports his view of the

polymeric character of the red sulphide. When heated carefully, the yellow and red sulphides undergo a series of changes of colour through which they pass on cooling in the reverse order, both returning to yellow, the red sulphide having suffered molecular disarrangement during the heating. When heated out of direct contact with the air they neither sublime nor oxidise beyond just the surface. The author finally goes into the question of cadmium pigments, finds zinc compounds the most ordinary adulterants, and gives various tests by which a good pigment for oil painting may be recognised.

D. A. L.

Action of Water on Lead. By M. MÜLLER (*J. pr. Chem.* [2], **36**, 317—340).—A sample of water from the Ocker was distilled. The amounts of dissolved gases and of ammonia were determined in the first, middle, and last fractions, and the behaviour of the different fractions with lead observed. The water before distillation contained 0·00015 per cent. of ammonia.

	First fraction.	Middle fraction.	Last fraction.
Ammonia	0·00115 p. c.	0·0001 p. c.	0·00008 p. c.

Dissolved gases reduced to 0° and 760 mm. pressure.

Total volume	2·04 vol. p. c.	1·196 vol. p. c.	0·77 vol. p. c.
Carbonic anhydride.....	1·159 "	0·178 "	0·025 "
Oxygen	0·269 "	0·316 "	0·232 "
Nitrogen (diff.)	0·612 "	0·702 "	0·513 "

The first fraction scarcely attacked polished strips of pure lead, which became slowly covered with a thin deposit. The water remained perfectly clear. The middle and last fractions acted very energetically, the lead was rapidly corroded, and the water became turbid. In order to ascertain whether the protecting influence of the first fraction was due to the ammonia or the carbonic anhydride it contained, well water, perfectly free from ammonia, was distilled, and the amount of gas dissolved in different portions of the distillate was ascertained.

	First fraction.	Middle fraction.	Last fraction.
Dissolved gases reduced to 0° and 760 mm. pressure.			
Total volume	2·661 vol. p. c.	1·312 vol. p. c.	1·047 vol. p. c.
Carbonic anhydride.....	2·030 "	0·218 "	0·069 "
Oxygen	0·198 "	0·358 "	0·341 "
Nitrogen (diff.)	0·433 "	0·738 "	0·637 "

In this case also the first fraction showed scarcely any action on lead, after remaining in contact with it for 24 hours. The middle and last fractions attacked it with considerable energy. The protecting influence of the first fractions must be considered as due to their con-

taining a relatively large quantity of carbonic anhydride. Distilled water, which was vigorously boiled for some time and quickly cooled in contact with air, was found to contain 0.04 per cent. of its volume of carbonic anhydride, 0.236 per cent. of its volume of oxygen, and 0.514 per cent. of its volume of nitrogen. The rapid absorption of these gases explains the behaviour of water so treated towards lead. Distilled water, quite free from carbonic anhydride but containing oxygen, scarcely acts on lead, but on exposure to the air the liquid becomes cloudy, owing to the formation of a white precipitate.

Samples of water containing different amounts of carbonic anhydride, but an invariable quantity of oxygen, behave very differently with lead. In one case, when the oxygen present was 0.35 per cent. of the volume of the liquid, and a saturated solution of carbonic anhydride was added until the water contained 0.14 per cent. of its volume, the lead was appreciably attacked. On increasing the carbonic anhydride to 0.6 vol. per cent., the attack became remarkably energetic. With 1 vol. per cent. the action was considerably weaker, and when the carbonic anhydride was increased to 1.5 vol. per cent. the lead was no longer visibly corroded. Water containing 2, 2.5, and 3 vols. per cent. of carbonic anhydride was equally inactive. Water containing carbonic anhydride but no oxygen is practically without action on lead, when atmospheric air is excluded. When strips of lead are immersed for eight days in pure distilled water, recently boiled and cooled out of contact with the air, they do not become tarnished. Before filtration, however, but not after, the water gives a considerable reaction with hydrogen sulphide. Pure water evidently attacks lead with formation of an oxide. Ordinary distilled water in which strips of lead were placed, and from which the air was excluded, contained a maximum quantity of lead at the end of three days, after which the lead was by degrees thrown out of solution. This is explained by supposing that water containing carbonic anhydride and oxygen in contact with lead forms lead carbonate, which dissolves in the excess of the gas; but as more lead oxide is formed, this carbonic anhydride is absorbed, and all the lead falls out of solution as lead carbonate. Distilled water, free from carbonic anhydride, to which minute quantities of ammonia have been added, attacks lead, but is without action on it if carbonic anhydride is present.

Lime water, through which a current of air, perfectly free from carbonic anhydride, was passed, at first slowly dissolved lead, but this was soon again thrown out of solution in the form of minute crystals. The solution attained a maximum after 13 hours, and then decreased. Sodium hydroxide solution behaved in a similar way. In the absence of oxygen, neither lime-water nor sodium hydroxide solution attacked lead. Lead tubing, buried in mortar, and kept in a dry room for a year suffered no change, but when the mortar was occasionally moistened with pure water, corrosion rapidly took place. When soapy water or an alkaline solution of lime was used instead of pure water, the decomposition-products consisted to some extent of red lead.

Ordinary distilled water, to which a small quantity of sodium carbonate was added, dissolved no lead, but the metal became slowly

covered with a white, compact coating. When the water contained oxygen but no carbonic anhydride, lead was found in solution after a few hours. A trace of sodium hydrogen carbonate added to distilled water completely prevented the dissolution of lead, and the metal became covered with a protecting crust. Waters containing lead in solution were found to be freed from it by adding sodium carbonate. Pure lead carbonate is soluble in water containing carbonic anhydride; it is reprecipitated by boiling the solution or by adding hydrogen sodium carbonate to it. Evidently lead forms an acid carbonate, which is soluble in water but possesses little stability. Hydrogen calcium carbonate acts in precisely the same way as hydrogen sodium carbonate.

Polished strips of lead immersed in a saturated solution of pure calcium sulphate, containing oxygen, become covered with a hard white coating, but no lead goes into solution. In the absence of oxygen, the metal remains perfectly bright. On placing lead covered with the white crust formed by long immersion in a solution of calcic sulphate, in pure distilled water, no lead went into solution except when a considerable quantity of carbonic anhydride was present. When a trace of hydrogen calcium carbonate was added to the solution, in no case was any lead dissolved. The coating is in all probability a basic sulphate of lead.

The presence of minute quantities of chlorides, nitrates, organic matter, and ammonia in water, did not influence its behaviour towards lead. This seems to depend on the presence of oxygen and carbonic anhydride. Water containing much organic matter, and rich in carbonic anhydride, rapidly corrodes lead, but polished surfaces of the metal remain perfectly bright when immersed in pure solutions of organic compounds, such as starch and sugar, provided no carbonic anhydride is present.

G. T. M.

Colloidal Copper Sulphide. By W. SPRING and G. DE BOECK (*Bull. Soc. Chim.*, **48**, 165—170).—An aqueous solution of copper sulphide can be obtained by precipitating any copper salt by hydrogen sulphide and washing by decantation with dilute sulphuric acid. As the impurities are removed, the copper sulphide becomes soluble and forms a dark-coloured solution with a slight greenish fluorescence. A purer product is obtained by precipitating with ammonium sulphide. The solution contains hydrogen sulphide and may possibly contain copper hydrosulphide. The former may be expelled by a short ebullition without any notable precipitation of copper taking place. Analysis of the liquid shows that the copper and sulphur are in the ratio required by the formula CuS , and hence the solution contains no copper hydrosulphide. Examination with the spectro-scope shows that the solution is a true solution and not simply a turbid liquid. It absorbs half the red, the violet, and half the blue in the spectrum of a lamp flame.

The copper sulphide is precipitated from this solution by the addition of various salts, a list of which is given in the paper, but the power of precipitation bears no simple relation to the molecular weight or molecular volume of the salt. The valency of the metal, however,

exerts considerable influence. Alum, chrome alum, and aluminium sulphate, precipitate it when added in very small quantities, and the precipitating power of salts of dyad metals is about 10 times as great as that of salts of sodium and potassium.

Schulze has made similar observations in the case of antimony sulphide, but the copper sulphide is more readily precipitated than the antimony compound.

C. H. B.

Stability of Mercuric Chloride Solutions. By V. MEYER (*Ber.*, 20, 2970—2974; comp. Abstr., 1887, 774).—Further experiments have shown that the solutions of mercuric chloride in the hard Göttingen water, even when preserved in hermetically sealed flasks with or without the addition of common salt, gradually deposit mercuric oxychloride, but less rapidly than when kept in vessels exposed to the air; atmospheric dust, however, does not seem to influence the rate of decomposition in any very marked way. If the solution of mercuric chloride in ordinary water, instead of being exposed to diffused daylight, is kept in the dark in well-stoppered flasks, it is found that practically no decomposition occurs, even after two months in solutions made with Göttingen water, pond water, and a well water charged with organic impurity, to which no addition of salt has been made; the very small amount of decomposition which actually occurs being attributed to the unavoidable exposure to diffused daylight during the repeated examination of the solutions.

W. P. W.

Action of Alumina and Kaolin on Calcium Chloride. By A. GORGEU (*Bull. Soc. Chim.*, 48, 51—52).—Calcium chloride mixed with alumina, kaolin, or ordinary clay, and fused at a cherry-red heat in presence of moist air, yields crystalline products soluble in dilute acids. With alumina, the crystals are distinct, colourless, mono-refractive, modified tetrahedra. They are anhydrous at 120°, have the composition $6\text{Al}_2\text{O}_3, 10\text{CaO}, \text{CaCl}_2$, and are slowly decomposed by boiling water. Kaolin alone, or mixed with silica, seems to produce various crystalline compounds, including mono-refractive crystals resembling calcium garnet, but these could not be isolated. After prolonged fusion, the product was treated with dilute hydrochloric acid and a solution of sugar. In this way modified tetrahedra of the composition $3\text{SiO}_2, 3\text{Al}_2\text{O}_3, 16\text{CaO}, 2\text{CaCl}_2$ were obtained. It would seem that calcium garnet is first formed, and afterwards converted into the chlorosilicate. Calcium garnet, in fact, when fused with calcium chloride and oxide, yields modified tetrahedra similar to those just described.

C. H. B.

Soluble Manganese Oxide. By W. SPRING and G. DE BOECK (*Bull. Soc. Chim.*, 48, 170—172).—This manganese oxide is obtained by acting on potassium permanganate with sodium thiosulphate, and thoroughly washing the precipitate with water. As soon as all the potassium has been removed, a brown solution is obtained, from which the oxide is precipitated on the addition of any salt (comp. Gorgeu, *Ann. Chim. Phys.* [3], 63, 155). Analysis of the product obtained by

evaporation of the brown solution shows that it has the composition $4(\text{MnO}_2, \text{H}_2\text{O}), \text{Mn}_3\text{O}_4$.

The portion of the original precipitate which is insoluble in water has the composition $\text{Mn}_3\text{O}_{13}, 4\text{H}_2\text{O}$, or $3\text{MnO}_2, \text{Mn}_3\text{O}_4, \text{Mn}_2\text{O}_3, 4\text{H}_2\text{O}$.

The colloidal manganese oxide is precipitated by salts more readily than colloidal copper sulphide, and the valency of the metals in the salts has the same influence in both cases. The manganese solution can be kept for a long time in sealed tubes, but if filtered through paper the manganese is completely precipitated. C. H. B.

Potassium Manganite. By A. JOLLES (*Chem. Zeit.*, **11**, 1394—1395).—In a previous communication, it is stated that the following equation: $\text{K}_2\text{MnO}_4 + \text{C}_2\text{H}_6\text{O} = \text{K}_2\text{MnO}_3 + \text{C}_2\text{H}_4\text{O} + \text{H}_2\text{O}$, represents the oxidation which takes place in the author's test for certain impurities in chloroform (Abstr., 1887, 866). This statement has been contested. It is now shown that both aldehyde and the manganite K_2MnO_3 are produced, but in excess of alcohol the latter soon decomposes; when, however, the substances are taken in equivalent quantities, the manganite can be separated and dried over sulphuric acid. It is a yellowish-brown substance; is decomposed by dilute nitric and sulphuric acids, yielding manganese dioxide and hydrated dioxide and potassium nitrate or sulphate. It oxidises sulphurous acid to sulphuric acid, which in the nascent state forms manganese sulphate. Boiled with oxalic or tartaric acid, the manganite dissolves with evolution of carbonic anhydride. On exposure to a current of superheated steam and air, it is partially converted into manganate (compare Rousseau, Abstr., 1887, 552, 892). D. A. L.

Manganese Compounds. By B. FRANKE (*J. pr. Chem.* [2], **36**, 451—468; compare Abstr., 1887, 893, 1016).—By heating 8 grams of potassium permanganate with 100 c.c. of strong sulphuric acid at 100° , and allowing it to cool, a brown crystalline salt, $\text{Mn}_2\text{O}_3, 4\text{SO}_3, 5\text{H}_2\text{O}$, is formed. When this is treated with water, it is decomposed into equimolecular quantities of manganous sulphate and the hydrated oxide H_2MnO_3 ; the salt is probably $\text{Mn}_2(\text{SO}_4)_3, \text{H}_2\text{SO}_4 + 4\text{H}_2\text{O}$.

Manganic sulphate, $\text{Mn}_2(\text{SO}_4)_3$, is obtained when the above salt is heated more strongly with sulphuric acid, in green crystals, decomposed by water in the same way as the acid salt, showing that the atoms of manganese are of different valency. The salt may therefore be regarded as the manganous salt of an acid, $\text{Mn}^{\text{iv}}\text{SO}_4(\text{O}\cdot\text{SO}_2\cdot\text{OH})_2$, analogous to the manganous manganese chloride (Abstr., 1887, 893). $\text{Mn}_2(\text{SO}_4)_3, \text{K}_2\text{SO}_4$ is obtained in red-brown crystals by carefully heating 8 grams of potassium permanganate with the mother-liquor from the above acid salt; water decomposes it in a manner similar to the other salts.

Steel-grey, metallic-looking crystals of $\text{H}_2\text{Mn}_2\text{O}_4$ are obtained when either of the foregoing compounds is thrown into very weak aqueous soda; sulphuric acid decomposes it into manganous sulphate and manganous acid, $\text{MnO}(\text{OH})_2$, which is thus obtained pure as a brown powder; this points to the formula $\text{Mn} < \overset{\text{O}}{\text{O}} > \text{Mn}(\text{OH})_2$.

The brown colour of the solution of manganese dioxide in strong hydrochloric acid is caused by the presence of manganous acid.

A. G. B.

Permanganates. By T. KLOBB (*Bull. Soc. Chim.*, **48**, 240—244).—The author has previously prepared certain permanganates by adding potassium permanganate to ammoniacal solutions of certain metallic salts (Abstr., 1886, 983). He has now obtained similar derivatives from luteocobalt chloride in a similar way.

Luteocobaltic permanganate, $\text{Co}_2(\text{MnO}_4)_6 \cdot 12\text{NH}_3$, is obtained by mixing warm concentrated solutions of luteocobalt chloride (1 mol.) and potassium permanganate (12 mols.) It separates in the form of a precipitate mixed with a salt which crystallises in hexagonal plates, and is formed in greater proportion when the permanganate is not in excess. The latter can be removed by treatment with cold water, and the luteocobaltic permanganate is recrystallised from water at 60° . It then forms very brilliant, black tetrahedra, only slightly soluble in cold water, but more soluble in hot water with partial decomposition. When heated, it detonates, and it also explodes when struck. With hydrochloric acid, it yields manganous chloride and luteocobaltic chloride.

Luteocobaltic chloropermanganate, $(\text{Co}_2 \cdot 12\text{NH}_3)\text{Cl}_4 \cdot 2\text{MnO}_4$, is prepared by mixing a solution of luteocobaltic chloride (8 mols.) with a solution of luteocobaltic permanganate (1 mol.), filtering rapidly, and allowing to cool. It separates in small, black lamellæ with the form of a regular hexagon, red or brown by transmitted light. It is very unstable, and is decomposed by water with removal of the chloride, but dissolves without decomposition in a solution of luteocobaltic chloride. When heated rapidly, it detonates, but it does not explode on percussion.

Luteocobaltic bromopermanganate is analogous to the chloropermanganate, and is prepared in a similar way, or more simply, by mixing warm solutions of potassium permanganate (3 mols.) and luteocobaltic bromide (1 mol.), and allowing them to remain. It forms brilliant, hexagonal lamellæ, which are much more stable than the chlorine-derivative, and are not decomposed by boiling water.

The salt which is obtained in the preparation of luteocobaltic permanganate, and which crystallises in hexagonal lamellæ, is also obtained by mixing cold concentrated solutions of luteocobaltic chloride (1 mol.) and potassium permanganate (3 mols.), when it separates slowly in violet hexagonal lamellæ of the composition $(\text{Co}_2 \cdot 12\text{NH}_3)\text{Cl}_2 \cdot 2\text{KCl} \cdot 4\text{MnO}_4$, very soluble in water with partial decomposition into its constituents. When heated, it behaves like the preceding salts. It may be regarded as a compound of luteocobaltic permanganate and luteocobaltic chloride with potassium chloride. It can also be formed by dissolving luteocobaltic chloropermanganate in potassium chloride solution, or by the action of luteocobaltic permanganate on a large excess of potassium chloride.

C. H. B.

Electrolytic Extraction of Antimony. By W. BOECHERS (*Chem. Zeit.*, **11**, 1021—1022).—The author has based a process for the extraction of antimony (from all its combinations soluble in sodium

sulphide solution) on the electrolytic method of Classen and Ludwig (Abstr., 1885, 932) for the estimation of that metal.

The ore is extracted with sodium sulphide solution, using 3 mols. Na_2S for every mol. Sb_2S_3 . The concentrated extract is mixed with 3 per cent. of sodium chloride to increase its conductivity, and electrolysed. According to the intensity of the current, the metal is deposited as a powder or in shining scales. To prevent deposition of sulphur, the relation of 1 atom of available Na for every atom of oxidisable sulphur must be maintained, but as the mixture $\text{Sb}_2\text{S}_3 + \text{Na}_2\text{S} + 2\text{NaHO}$ is too unstable, the above proportions are used; too much sodium sulphide is to be avoided as it increases the resistance of the liquid.

The common salt is easily crystallised from the electrolysed solutions, and the sulphur recovered as sodium thiosulphate without much difficulty.

D. A. L.

Antimoniates. By G. v. KNORRE and P. OLSCHESKY (*Ber.*, **20**, 3043—3052).—Attempts were made to prepare Fremy's potassium antimoniate, $\text{K}_4\text{Sb}_2\text{O}_7$ (*J. pr. Chem.*, **45**, 209), but without success; it is concluded that that salt does not exist, and that Fremy's compound is a mixture of potassium antimoniate and potash.

Potassium antimoniate, $\text{K}_2\text{Sb}_2\text{O}_6$, contains 5 mols. H_2O when air-dried, and is a white granular salt. 100 parts of water at 20° dissolve 2.81 parts of anhydrous salt. Sp. gr. of saturated solution at $18^\circ = 1.0263$. A table is given showing the loss of weight it undergoes at various temperatures; at 330° it contains rather more than 1 mol. H_2O , and the author assumes that 1 mol. H_2O is chemically combined, and that the formula of the air-dry salt is $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7 + 4\text{H}_2\text{O}$. When the hot aqueous solution is evaporated, a gummy salt remains; when this is dried at 100° , it has the composition expressed by the formula $\text{K}_2\text{Sb}_2\text{O}_6 + 3\text{H}_2\text{O}$.

Potassium antimoniate was also prepared by the methods of Brunner (*Dingl. polyt. J.*, **159**, 356) and Reynoso (*Annalen*, **80**, 272); details of preparation and results are given (compare Abstr., 1885, 1184).

N. H. M.

Mineralogical Chemistry.

Arksutite from Ivigtut in Greenland. By A. E. NORDENSKIÖLD (*Zeit. Kryst. Min.*, **13**, 400—401, from *Geol. Fören. Förhandl.*, **8**, 172—175).—A specimen of arksutite was separated according to Thoulet's method, and gave three different substances: an optically isotropic mineral having a sp. gr. of 3.12 (fluorspar); a mineral lighter than 2.99 (possibly thomsenolite); and a birefractive substance of sp. gr. = 2.994, and giving on analysis the following results:—

Al.	Ca.	Mg.	Na.	F.	Total.
17.28	0.22	0.05	24.72	57.16	99.43

corresponding with the formula $5\text{NaF} + 3\text{Al}_2\text{F}_3$. The composition of arksutite is thus perfectly in accord with that of the chiolite of Brandl. From the optical properties of the two minerals, there can be no doubt that they are identical.

B. H. B.

Mineralogical Notes. By G. FLINK (*Zeit. Kryst. Min.*, **13**, 401—408, from *Bihang till K. Sv. vet. akad. handl.*, **12**, Afd. 2).—The author gives the results of a crystallographical and chemical investigation of the following minerals:—1. Cobalt-glance from Nordmarken; 2. Cosalite from Nordmarken; 3. Pyrochroite from Nordmarken; 4. Magnetite from Nordmarken; 5. Manganomagnetite from Långban; 6. Berzeliite from the same locality; 7. Monimolite from Pajsberg; 8. Xenotime from Hitterö, Norway; 9. Apatite from Nordmarken; 10. Liévrte from Thyrril, Iceland; 11. Epidote from Nordmarken (28 new planes); 12. Epidote from Mörkhult; 13. Manganese-vesuvian from Pajsberg; 14. Orthoclase from the krafite of Krafla, Iceland; 15. Titanite from the Fredriksberg Mine, Nordmarken.

The author also describes a new mineral, *harstigitite*, from Pajsberg, named after the mine in which it was discovered. The mineral belongs to the rhombic system, and exhibits the forms ∞P , $\infty \bar{P}\infty$, $\bar{P}\infty$, $\infty \bar{P}2$, $\infty \bar{P}\infty$, $\bar{P}2$. $a : b : c = 0.7141 : 1 : 1.01495$. No cleavage was observed. The mineral is colourless, and has a vitreous lustre. Analysis gave the following results:—

SiO_2 .	Al_2O_3 .	CaO .	MnO .	MgO .	K_2O .	Na_2O .	H_2O .	Total.
38.94	10.61	29.23	12.81	3.27	0.35	0.71	3.97	99.89

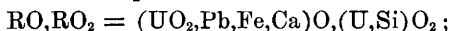
B. H. B.

Manganese and Uranium Oxides. By C. RAMMELSBURG (*Zeit. Kryst. Min.*, **13**, 418—419, from *Ber. Akad. Ber.*, 1885, 97).—The author finds that both artificial Mn_3O_4 and crystallised hausmannite, when boiled with concentrated nitric acid, or treated with dilute sulphuric acid, split up into 2MnO , which dissolves, and insoluble MnO_2 . Crystallised manganite is not decomposed by sulphuric acid in the same way. Powdered braunite undergoes decomposition, although not completely. Hausmannite should therefore be regarded as having the composition $2\text{MnO}, \text{MnO}_2$, whilst the formula of braunite is $\text{MnO}, (\text{Mn}, \text{Si})\text{O}_2$.

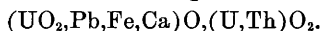
The author gives the following new analysis of pitchblende from Joachimsthal:—

UO_3 .	UO_2 .	PbO .	FeO .	CaO .	SiO_2 .	Total.
42.87	40.50	3.25	3.78	3.00	6.60	100.00

The general formula of pitchblende is



the formula of the varieties containing thorium is



The oxides, Y_2O_3 , Er_2O_3 , Ce_2O_3 , which occur in several varieties of pitchblende, appear to be isomorphically mixed with the compound

RO, RO_2 . The latter is thus analogous in constitution to braunite, which crystallises in a similar manner. B. H. B.

Minerals from Carinthia. By A. BRUNLECHNER (*Zeit. Kryst. Min.*, 13, 391—392, from *Jahrb. nat. hist. Landesmuseums in Kärnthen*, 17, 1—5).—Among the Carinthian minerals described by the author are the following:—Greenockite from Raibl, as a lemon-yellow coating on slate; garnet from Lamprechtsberg in the Lavanthal, as orange crystals enclosing copper pyrites; tourmaline from the same locality, in short, dark-brown crystals; zoisite from Stanziwurdkopf, green in columnar crystals in mica schist. Analyses are given of two specimens of siderite: I. Translucent crystals, with plane faces, from Wölch; II. Yellowish-white crystals, with curved faces, from Lölling:—

	FeCO_3 .	MnCO_3 .	MgCO_3 .	CaCO_3 .	Impurities.	Total.
I.	95·10	2·11	2·19	trace	0·59	99·99
II.	94·97	trace	3·22	1·78	0·25	100·22

In addition to other factors, the proportion of calcium, even in small quantities, appears to influence the crystal form of iron carbonate. B. H. B.

Martinite from the West Indies. By J. H. KLOOS (*Jahrb. f. Min.*, 1888, i, Ref., 41, from *Sammlg. geol. Reichsmuseums, Leiden*).—Martinite is a new calcium phosphate pseudomorphous after gypsum, from the phosphorite beds of the Island of Curaçao. The pseudomorphs occur in lenticular crystals, having the form of gypsum ($-\text{P}$, $-\text{P}\infty$, $\infty\text{P}\infty$). The crystals are colourless and transparent. Their sp. gr. is 2·892 to 2·896. Analysis gave the following results:—

P_2O_5 .	CaO .	Loss on ignition.	Total.
47·87	47·63	5·46	100·96

Fluorine is absent. The results of the analysis are in accord with the empirical formula $10\text{CaO}, 4\text{P}_2\text{O}_5, 3\text{H}_2\text{O}$. B. H. B.

Diadochite from Visé. By G. CESÀRO (*Zeit. Kryst. Min.*, 13, 421—422, from *Ann. soc. géol. Belg.*, 12, 173).—The mineral from Visé, to which the name *destinézite* has been assigned, appears to be a variety of diadochite. An almost white and very pure specimen gave on analysis the following results:—

Fe_2O_3 .	P_2O_5 .	SO_3 .	H_2O .	Hygroscopic H_2O .	C.	Total.
37·60	16·76	18·85	25·35	0·30	1·40	100·26

The mineral on microscopic examination was found to belong to the monoclinic system. B. H. B.

Mineral from Krems in Austria. By E. DRASCHE (*Jahrb. f. Min.*, 1888, i, Ref., 29—30, from *Verh. geol. Reichsanst.*, 19, 81).—The

author gives an analysis of a mineral, erroneously supposed to be bauxite, which is found in considerable quantities interbedded in crystalline schists. The mineral is of a white to yellowish-brown colour. For the analysis, pure white specimens were selected. The results were as follows :—

SiO ₂ .	Al ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	SO ₃ .	P ₂ O ₅ .	H ₂ O at 100°.
1·30	38·00	0·75	3·75	4·54	38·85	0·88	0·45

The remainder consists of water and organic substance.

B. H. B.

Manganotantalite from the Ural. By A. ARZRUNI (*Jahrb. f. Min.*, 1888, i, Ref., 18, from *Trans. Imp. Russ. Min. Soc.*).—The crystal described was found in the Bakakin gold washings in the Sanarka district, in the south of the Ural. It exhibits the planes $\infty P\infty$, $\infty \bar{P}\infty$, OP , $\frac{1}{2}P\infty$, $\frac{1}{4}P\infty$, $P2$, $\frac{1}{2}P2$. It is semi-metallic and nearly black. In very thin layers the colour is orange to ruby-red. Sp. gr. = 7·37. Analyses gave the following results :—

Ta ₂ O ₅ .	Nb ₂ O ₅ .	SnO ₂ + WO ₃ .	FeO.	MnO.	CaO.	Ignition.	Total.
79·81	4·47	0·67	1·17	13·88	0·17	0·16	100·33

These results correspond with the formula $11MnTaO_6 + FeNbO_6$. This mineral, of which as yet only one crystal has been found, is the member of the tantalite group richest in manganese and tantalum.

B. H. B.

Kainosite, a new Mineral from Hitterö, in Norway. By A. E. NORDENSKIÖLD (*Zeit. Kryst. Min.*, 13, 399—400, from *Geol. Fören. Förhandl.*, 8, 143—146).—In consequence of the unusual composition of this new mineral, the author has termed it kainosite from *καίνος* (strange). It consists of a calcium yttrium silicate, mixed with a carbonate and water. The only specimen found is a portion of a hexagonal prism. The optical examination, however, shows that it belongs, not to the hexagonal, but to the rhombic or to the monoclinic system. The mineral is semi-transparent, yellowish-brown, and birefractive. Its hardness is 5·5, and sp. gr. 3·413. Analysis gave the following results :—

SiO ₂ .	Y ₂ O ₃ + Er ₂ O ₃ .	CaO.	MgO.	FeO.	Na ₂ O.	CO ₂ .	H ₂ O.	Total.
34·63	37·67	15·95	0·03	0·26	0·40	5·90	5·26	100·10

corresponding with the formula $4SiO_2.CO_2.Y_2O_3(Er_2O_3).2CaO.2H_2O$.

B. H. B.

Chemical Nature of Eudialite. By C. RAMMELSBERG (*Jahrb. f. Min.*, 1887, ii, Ref., 449—451, from *Sitzber. K. Preuss. Akad. Wiss.*, 24, 441—461).—The author has analysed specimens of this rare silico-zirconate from the principal localities at which it is found. The results of his analyses were as follows :—

	Cl.	SiO ₂ .	ZrO.	Ce ₂ O ₃ .	FeO.	MnO.	CaO.
I.	1.53	49.84	14.01	2.35	5.96	0.64	10.77
II.	1.57	48.88	15.17	4.07	7.28	0.52	10.63
III.	1.70	46.68	15.43	—	7.32	2.82	11.76
IV.	1.44	46.84	16.09	5.19	5.92	1.50	10.52

	Na ₂ O.	K ₂ O.	H ₂ O.	Sp. gr.
I.	13.32	0.75	1.24	2.928
II.	8.80	1.24	2.50	2.908
III.	11.24	0.42	0.90	3.081
IV.	10.70	0.50	1.77	3.000

I. Eudialite from Kangerdluarsuk, Greenland; II. From Brevig, Norway; III. From Sigterö, Norway; IV. From Arö, Norway. The formula given by the author for the eudialite of Greenland and of Brevig is $\text{NaCl}, 2\text{R}'_6\text{R}''_3(\text{Si}, \text{Zr})_{10}\text{O}_{26}$, and for the eudialite of Sigterö and Arö is $\text{NaCl}, \text{R}'_{12}\text{R}''_9(\text{Si}, \text{Zr})_{25}\text{O}_{65}$. B. H. B.

Zeolites from Chili. By L. DARAPSKY (*Jahrb. f. Min.*, 1888, i, Mem., 65—67).—The author has subjected various zeolites, from the mineralogical collection of the National Museum of Santiago, to chemical examination. The analytical results were as follows:—

	SiO ₂ .	Al ₂ O ₃ .	CaO.	Na ₂ O.	H ₂ O.	K ₂ O.	Fe ₂ O ₃ .	Total.
I.	52.67	19.80	11.25	—	16.29	—	—	100.01
II.	54.60	—	29.52	1.06	15.03	—	—	100.21
III.	47.69	25.45	14.05	—	13.25	—	—	100.44
IV.	46.74	25.99	9.11	5.23	12.41	—	—	99.48
V.	45.15	26.53	11.86	2.24	13.81	0.45	—	100.04
VI.	43.57	24.27	21.74	0.96	5.28	—	4.44	100.26

I. Hypostilbite from altered amygdaloidal porphyry at the Hacienda La Quinta at Curicó; formula, $2\text{CaO}, 2\text{Al}_2\text{O}_3, 9\text{SiO}_2, 9\text{H}_2\text{O}$. II. Okenite from the Rio Putagan; formula, $2\text{CaO}, 3\text{SiO}_2, 3\text{H}_2\text{O}$. This appears to be identical with the zeolite from Greenland termed bordite by Dufrénoy. III. Scolezite, accompanying the okenite; sp. gr. 2.15; formula, $\text{CaO}, \text{Al}_2\text{O}_3, 3\text{SiO}_2, 3\text{H}_2\text{O}$. IV. Typical mesolite from the Desert of Atacama. V. A dense form of the same mineral coating the weathered rock of the Rodaito Mines in the Province of Coquimbo. VI. Prehnite, in green globular masses, from the Rodaito Mines, associated with calcite crystals, and containing small, black scales or wires of natural amalgam (Ag_{39}Hg). B. H. B.

Manganese-bearing Idocrase from Sweden. By L. J. IGELSTRÖM (*Jahrb. f. Min.*, 1887, ii, Ref., 453, from *Bull. soc. franç. min.*, 9, 22—24).—The mineral occurs with manganese-garnet, manganese-epidote, and manganese-silicate in limestone at the Jakobsberg manganese mine in Wermland. The crystals exhibit the forms 0P , ∞P , $\infty\text{P}\infty$, P . In thick plates, the colour is black; in powder, dark-violet. In thin sections, the mineral is highly pleochroic, having an amethyst and orange colour. In chemical composition it is character-

ised by a remarkably high percentage of manganese, copper, and lead, as is shown by the following analytical results:—

SiO ₂ .	Al ₂ O ₃ .	FeO.	MnO.	CuO.	PbO.	CaO.	MgO.	Total.
38·07	15·88	5·08	4·72	2·16	1·80	25·60	5·07	98·38

B. H. B.

Beryl from Madagascar. By A. DAMOUR (*Jahrb. f. Min.*, 1888, i, Ref., 9, from *Bull. soc. franç. min.*, 9, 153—154).—The crystal described was found with tourmaline, quartz, and triphane at Farafatrana, on the east coast of Madagascar. It is characterised by its pink colour. Its composition is as follows:—

SiO ₂ .	Al ₂ O ₃ .	BeO.	FeO.	MnO.	CaO.	Ignition.	Total.	Sp. gr.
66·56	18·66	12·47	0·09	0·21	0·06	2·30	100·35	2·72

B. H. B.

So-called Soda Granites. By A. GERHARD (*Jahrb. f. Min.*, 1887, ii, Mem., 267—275).—Although in the analyses of most granites, the percentage of potash exceeds that of soda, yet certain granites are known in which the opposite is the case. Attention was first drawn to such granites in 1856 by Haughton, who termed them *soda-granites*. The author has made a series of careful analyses of typical examples of these rocks, and finds that in the granites of Baveno, both the red and the white varieties, and in those of Bejby in Sweden, the soda is not, as stated by former observers, in excess of the potash. These rocks, consequently, should no longer be regarded as soda-granites.

In the granite of Ulferud, in Sweden, the author finds 74·77 per cent. of silica, 2·65 per cent. of potash, and 4·40 per cent. of soda, thus confirming the results obtained by Hummel and Erdmann. This rock is thus a true soda-granite. In addition to microcline, orthoclase, quartz, muscovite, biotite, zircon, and apatite, it contains a plagioclase-felspar, which gave on analysis the following results:—

SiO ₂ .	Al ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	Total.	Sp. gr.
67·99	19·23	1·84	1·25	9·69	100·00	2·63

and must therefore be regarded as an almost pure albite.

B. H. B.

Albite in Norwegian Pegmatites. By A. LACROIX (*Jahrb. f. Min.*, 1887, ii, Ref., 455, from *Bull. soc. franç. min.*, 9, 131—134).—The albite in the pegmatite veins of Moss, Hitterö, and Ytterby is always implanted on microcline, and is accompanied by quartz, calcite, and a mica differing from the muscovite of the rock. The crystals are poorly developed, the predominating form being ∞P_{∞} . Bands of albite contained in the microcline appear to be younger than that mineral. An analysis of the albite of Garta near Arendal gave the following results:—

SiO ₂ .	Al ₂ O ₃ .	Na ₂ O.	K ₂ O.	Total.	Sp. gr.
68·40	19·89	10·69	0·90	99·88	2·601

B. H. B.

Griqualandite. By B. H. BROUGH (*Chem. News*, 56, 244).—The author shows that the analysis of the supposed new mineral described

by Hepburn (Abstr., 1887, 709) as griqualandite, corresponds more closely with the simple formula $\text{H}_2\text{O}, \text{Fe}_2\text{O}_3, 4\text{SiO}_2$, than with the more complicated formula given. The percentage compositions demanded by the two formulæ are—

	SiO_2 .	Fe_2O_3 .	H_2O .
$\text{H}_2\text{Fe}_2\text{Si}_4\text{O}_{12}$	57·42	38·28	4·30
$\text{H}_{10}\text{Fe}_8\text{Si}_6\text{O}_{25}$	56·80	37·87	5·33

The formula $\text{H}_2\text{O}, \text{Fe}_2\text{O}_3, 4\text{SiO}_2$ for griqualandite is analogous to that of crocidolite, aegirine, and arfvedsonite, $\text{Na}_2\text{O}, \text{Fe}_2\text{O}_3, 4\text{SiO}_2$. Griqualandite must therefore be regarded as a crocidolite in which hydrogen is substituted for sodium. It is not a pseudomorph after crocidolite, but rather a fibrous hornblende or uralite resulting from the alteration of that mineral.

B. H. B.

Mineral Veins. By F. SANDBERGER (*Zeit. Kryst. Min.*, 13, 409—417).—This memoir is an abstract of the second volume of the author's treatise on mineral veins, in which he brings forward further evidence in support of the lateral secretion theory of the genesis of mineral veins. This theory assumes that water percolating through the country-rock has, by the aid of carbonic acid and other natural solvents, dissolved out of it all the minerals now forming the constituents of mineral veins. The greater portion of the volume is occupied by a discussion of the genesis of mineral veins in crystalline and stratified rocks.

In discussing the tin-ore veins in lithionite-granite, the author applies the term *protolithionite* to a dark lithium mica found in the granite masses of Cornwall, the Erzgebirge, and the Fichtelgebirge. In this mica, as much as 0·22 per cent. of tin oxide has been detected. The deposition of the tin ore, of zinnwaldite, and of turmaline in fissures in the granite is due to the decomposition of this mica. Prosopite is formed by the action of dissolved calcium carbonate on topaz. The fluorine derived from the mica explains the presence of fluorspar in the veins. Tin has also been detected in the potassium-mica of Villeder in Morbihan, and consequently the author regards the tin-ore veins of that district as formed by lateral secretion, whilst he regards the tin ore in the pegmatite of Finbo, in the beds of Pitkäranta and Breitenbrunn, as primitive. At Marienberg in Saxony, tin-ore veins occur in gneiss. In their formation by being dissolved out of the mica in the country-rock, the constituents, silica and tin oxide, least soluble in alkaline carbonates, were deposited first; then followed arsenic and copper; then cobalt and nickel ores, barytes (derived from the orthoclase of the country-rock); and lastly calcite and silver ores. Secondary mica is absent. In the mica of the mica-schist of Ehrenfriedersdorf, which is traversed by tin-ore veins, tin, arsenic, and fluorine have been detected. Lastly, small quantities of tin have been discovered in the phyllites of various districts. In those of Eibenstock and Johanngeorgenstadt, boron has also been found. This discovery enables the formation of interstratified turmaline-schist in these phyllites to be explained. The tin-ore deposits in

limestone at Campiglia were undoubtedly derived from an eruptive rock in the vicinity.

The Freiberg gneiss is extremely rich in mica, and in this mineral the majority of the metals occurring in the veins of that district have been detected. The barytes, however, appears to have been derived from the felspar of the country-rock. The metals contained in eruptive rocks of recent age, for instance, in the basalt of Strieth and in the phonolite of Hohenkrähen, segregate in fissures as magnetic or iron pyrites or as hydrated ferric oxide. The ore veins of Transylvania and of America are thought by the author to have been formed in a similar manner by leaching out of the andesites, &c. In the micas of Hungarian rocks, all the metals occurring in the mineral veins are found, whilst fluorine is absent. This is in accord with the known rare occurrence of fluorspar in those veins. The barytes is derived from the anorthic felspar of the country-rocks. At the Comstock lode, the lateral secretion theory has been confirmed by the discovery of the precious metals in the augite of the country-rock. The mineral veins of Caracoles in Jurassic limestone have been derived from the adjacent quartz-trachyte. The metals in this rock are contained for the most part in the hornblende, whilst in the felspar is contained a considerable proportion of barium, which appears in the veins as barytes.

B. H. B.

Composition of the Meteorite of Saint-Denis-Westrem. By C. KLÉMENT (*Jahrb. f. Min.*, 1888, i, Ref., 45, from *Bull. mus. roy. hist. nat. Belg.*, 4, 273—282).—The analysis of the meteorite from Saint-Denis-Westrem in East Flanders, gave the following results:—

SiO ₂ .	Al ₂ O ₃ .	Cr ₂ O ₃ .	FeO.	CaO.	MgO.	Na ₂ O.
40·20	2·54	0·10	16·22	2·00	25·08	0·99
Fe.	Ni.	Co.	S.	Total.		
10·37	1·24	0·12	2·12	101·78		

From these results, the author calculates the following mineralogical composition:—Chrome-iron, (FeCr₂O₄), 1·33; iron sulphide, (Fe₇S₈), 5·37; nickel-iron, 8·48; bronzite, 26·18; olivine, 46·41. The remaining 14·01 per cent., which consists of—

SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	Na ₂ O.
7·88	2·54	2·00	0·60	0·99

may perhaps be plagioclase (maskelynite).

B. H. B.

Mineral Springs in the Peninsula of Methana. By A. K. DAMBERGIS (*Ber.*, 20, 3328—3330).—The sulphur springs of Methana rise on the coast on the east side of the Chelona range near the village of Wromolimni, at about the sea level. The temperature of the water—which rises in more than 24 springs forming three separate groups—varies from 26·4° to 31°; the specific gravity of the water varies from 1·02865 to 1·02882. The water, when examined under the

microscope, was found to contain the bacteria *Beggiatoa nivea*, often found in sulphurous waters. The water from the various springs showed almost identical composition. The analysis of water from one of the springs gave in parts per 10,000:—NaCl, 297·630; KCl, 6·960; MgCl₂, 36·948; MgBr₂, 0·584; CaSO₄, 21·357; MgSO₄, 18·486; CaCO₃, 4·600; MgCO₃, 2·250; Fe₂O₃, 0·038; Al₂O₃, 0·019; SiO₂, 0·485; organic matter, 0·042; total solids, 389·399. CO₂ as bicarbonate, 3·200; CO₂ free, 7·218; SH₂, 0·109; total mineral constituents, 399·926. Besides this the water contained traces of ammonia, nitric acid, phosphoric acid, iodine, and fluorine.

L. T. T.

Analyses of Water from Artesian Wells. By C. KLÉMENT (*Jahrb. f. Min.*, 1888, i, Ref., 71—72, from *Bull. mus. roy. hist. nat. Belg.*, 3, 1—97).—The wells investigated are in Brussels or its immediate vicinity. The bore-holes struck water, below a bed of clay, in fissured chalk underlain by rocks of Silurian age. The following are the depths and temperatures of the water:—1. Hospital St. Pierre, Rue Haute, Brussels, 94·5 m., 15·2°; 2. Distillery, St. Gilles, 65·62 m., 11·8°; 3. Candle factory, Cureghem, 73 m., 12·5°; 4. Godin foundry, Laeken, 106·9 m., 12·5°; 5. St. Sauveur baths, Brussels, 75 m., 12·8°; 6. Boeck brewery, Koekelberg, 115·5 m., 12·0°; 7. Brewery, Anderlecht, 95 m., 12·2°; 8. Starch manufactory, Machelen, 82 m., 12·5°. The analyses were conducted in accordance with Bunsen's method with the following results:—

	1.	2.	3.	4.	5.	6.	7.	8.
CaCO ₃	0·1343	0·1902	0·0852	0·1084	0·1811	0·0679	0·0998	0·1295
MgCO ₃	0·0228	0·0740	0·0425	0·0593	0·0976	0·0362	0·0492	0·0686
Na ₂ CO ₃	0·0313	0·0170	—	0·0569	0·0606	0·0653	0·0140	0·0726
K ₂ NO ₃	0·0009	0·0010	0·0020	0·0021	0·0016	0·0014	0·0008	trace
K ₂ SO ₄	0·0388	0·0167	—	0·0256	0·0174	0·0263	0·0374	0·0263
CaSO ₄	—	—	0·0286	—	—	—	—	—
MgCl ₂	—	—	0·0174	—	—	—	—	—
NaCl	0·0276	0·0063	0·4618	0·0490	0·0020	0·1980	0·4409	0·0102
KCl	0·0008	0·0106	0·0433	0·0175	0·0230	0·0177	0·0093	0·0233
SiO ₂	0·0324	0·0200	0·0257	0·0300	0·0320	0·0302	0·0258	0·0302
Org. subs.	0·0449	0·0179	0·0173	0·0178	0·0135	0·0160	0·0245	0·0115
CO ₂	0·0840	0·1295	0·0598	0·1024	0·1559	0·0759	0·0755	0·1231
CO ₂ free	0·0065	0·0250	0·0274	0·0074	0·0143	0·0032	0·0045	0·0084

B. H. B.

Organic Chemistry.

Preparation of Trimethylene. By G. GUSTAVSON (*J. pr. Chem.* [2], 36, 300—303).—Trimethylene may be prepared by heating trimethylene bromide with zinc-dust and aqueous alcohol or water; 1 litre of the gas is thus obtained from 10 grams of bromide, and from this quantity of the gas 7.2 grams of dry, crude trimethylene bromide (or 4.57 grams iodide) can be again produced, showing that this method of preparation gives good results.

When trimethylene is passed into concentrated sulphuric acid, liquid hydrocarbons are formed on the surface of the acid, and the solution, after diluting, yields normal propyl alcohol on distillation.

F. S. K.

Conversion of Trimethylene Bromide into Propylene Bromide. By G. GUSTAVSON (*J. pr. Chem.* [2], 36, 303—304).—When trimethylene bromide and aluminium bromide are placed together in a sealed tube at the ordinary temperature, the former undergoes intermolecular change and propylene bromide is formed.

F. S. K.

Ethylpropylacetylene. By A. BÉHAL (*Bull. Soc. Chim.*, 48, 216—219).—Butyrene (106 grams) is gradually mixed with phosphorus pentachloride (200 grams), and when the action has ceased a further quantity of butyrene is added and the reaction is completed by heating. The liquid is then cooled and poured on ice, and the chlorine-derivative separated and heated with alcoholic potash in sealed tubes at 130—150° for 20 hours. The product is treated with water and dried over calcium chloride. The ethylpropylacetylene thus obtained is a liquid which boils at 105—106°, and has an odour of acetylene; sp. gr. at 0° = 0.760.

It does not combine with cuprous chloride, but with mercuric chloride a white precipitate is formed after some time, and when this precipitate is dissolved in dilute hydrochloric acid an odour of butyrene can be perceived.

Bromine acts on it with great energy, yielding a liquid of higher sp. gr. than water. When treated with about twice its own weight of concentrated sulphuric acid at 0°, the hydrocarbon yields a red-brown solution which becomes colourless when mixed with ice. The sole product of hydrolysis is butyrene.

The removal of 2 mols. of hydrogen chloride from dichlorobutyrene may yield diethylallylene, or the corresponding hydrocarbon with a closed chain, but the fact that this hydrocarbon forms a compound with mercuric chloride, and is readily hydrolysed, combined with the absence of tertiary carbon united with the carbon which is in union with the chlorine, render it most probable that this hydrocarbon is ethylpropylacetylene, $\text{CEt}:\text{CPr}$.

C. H. B.

Hydrolysis of Diallyl. By A. BÉHAL (*Bull. Soc. Chim.*, **48**, 43—51).—Diallyl is added drop by drop with continual agitation to ordinary concentrated sulphuric acid cooled by ice. The acid becomes red but the colour disappears when the acid is diluted by ice, which is added in sufficient quantity to reduce the temperature, and the product is then neutralised with an alkali or an alkaline earth, preferably the former. The liquid is then distilled and the supernatant layer separated. In all cases the sulphonic acid, $C_6H_{11} \cdot SO_3H$, is obtained. The barium, calcium, and potassium salts are very soluble in water and crystallise with difficulty.

The supernatant layer of the distillate boils at 93° , and is soluble in 15 parts of water at the ordinary temperature. It does not combine with sodium hydrogen sulphite even after prolonged contact, has no action on hydroxylamine, and does not reduce ammoniacal silver nitrate in alcoholic or aqueous solution. It dissolves in hydrochloric acid with development of heat, but no combination takes place; when heated with this acid in sealed tubes at 143 — 150° , it yields dichlorhydrin boiling at 170 — 180° . It does not precipitate magnesium chloride solutions, and when treated with phosphorus pentachloride a considerable quantity of hydrogen chloride is evolved, but no definite products could be isolated. Bromine is absorbed with great energy, but the product readily decomposes and cannot be distilled even in a vacuum. In one case the liquid was treated with excess of bromine and then washed with water; when the water was added there was considerable development of heat, and the liquid separated into two layers. The lower layer was hexylene bromide, probably corresponding with pseudo-hexylene glycol. The upper aqueous liquid readily reduced ammoniacal silver nitrate, and when neutralised and distilled yielded a small quantity of a liquid having the properties of an aldehyde.

The original liquid heated with water at 150 — 180° yields no glycol.

When hexyl pseudoglycol is mixed with concentrated sulphuric acid at 0° , it yields a product identical with that obtained by the action of the acid on diallyl.

The hydrolysis of diallyl under the influence of sulphuric acid yields a compound formed by the dehydration of isohexyl glycol, identical with the hexylene pseudoxide obtained by Wurtz by the action of silver oxide on diallyl dihydriodide. The oxide thus obtained differs from ordinary glycol by its inaptitude to combine with water, and has the constitution $\begin{matrix} CH_2 \cdot CHMe \\ < \\ CH_2 \cdot CHMe \end{matrix} > O$. Its formation is due to the fact that the two alcoholic groups from which the oxide is derived are separated by two atoms of carbon; and the two ethylene-groups do not act independently, but have been linked together by the atom of oxygen, forming an oxide more stable than the glycol. Moreover, the hydroxyl-groups in pseudo-hexyl glycol are in the γ position, and hence readily form an anhydride.

The other products of the hydrolysis are a sulphonic acid and polymerides of diallyl.

C. H. B.

Pyrrolylene Tetrabromide. By G. CIAMICIAN (*Ber.*, **20**, 3061—3064).—The author considers the explanation given by Grimaux and Cloëz (*Abstr.*, 1887, 789) to be improbable.

Hydrocyanic Acid and Cyanogen Iodide. By E. v. MEYER (*J. pr. Chem.* [2], **36**, 292—299). The author confirms Millon's statement that small quantities of hydrocyanic acid prevent the reduction of iodic acid by formic acid, and finds that the hydrocyanic acid causes the iodic acid to assume a passive state, since even when all the former acid has been expelled from the solution by boiling, a certain time elapses before the iodine begins to separate. On the other hand, hydrocyanic acid does not prevent, but only checks, the reduction of iodic acid by sulphurous acid, and a considerable quantity of the latter must be added before the separation of iodine commences. Hydrocyanic acid has no influence on the reduction of iodic acid by hydriodic acid. When a solution of iodine is added to hydrocyanic acid, cyanogen iodide and hydriodic acid are formed up to a certain point, after which the iodine is no longer acted on. These two products have a great tendency to reproduce hydrocyanic acid and iodine, but an excess of hydrocyanic acid prevents this inverse change taking place. Numerous experiments were made to find how much iodine must be added to a constant quantity of hydrocyanic acid in varying quantities of water before free iodine is present in the solution, and the tabulated results show that the amount of iodine used increases with dilution and with the temperature. Cyanogen iodide is completely decomposed by hydriodic acid and sulphurous acid, and these reactions may be employed for the estimation of cyanogen iodide volumetrically. Hydrogen sulphide, stannous chloride, and other reducing agents act in like manner, but towards oxidising agents cyanogen iodide is as stable as iodic acid.

F. S. K.

Oxidation of the Azulmic Matter obtained by the Electrolysis of Ammonia with Carbon Electrodes. By A. MILLOT (*Bull. Soc. Chim.*, **48**, 238—240).—The composition of the black residue obtained by evaporating the liquid after electrolysis (*Abstr.*, 1886, 979), then extracting with alcohol, and finally with water is—C, 35.5; H, 2.0; N, 36.3; O, 26.2. It is not readily oxidised by sodium hypochlorite.

10 grams of the residue was dissolved in water and ammonia, the ammonia expelled by heating on the water-bath, and the gelatinous residue mixed with 50 c.c. of hydrogen peroxide capable of giving 3000 c.c. of oxygen. The mixture was heated on the water-bath for 10 or 12 hours and filtered. On cooling, ammelide is deposited, and on further concentration a second quantity of this compound is obtained. The mother-liquor is evaporated to dryness and extracted with alcohol, which when concentrated deposits crystals of cyanuric acid. The last extracts yield nacreous plates or rhomboïdal prisms of the hydrated acid resembling the modification which Liebig termed cyanilic acid. When this is dissolved in sulphuric acid and precipitated by adding water, it separates in the ordinary form.

That portion of the products of oxidation which is insoluble in

alcohol consists of ammonium sulphate, the sulphuric acid having been present as an impurity in the hydrogen peroxide. C. H. B.

Sulphuranes. By E. BRAUN (*Ber.*, **20**, 2967—2970).—When ethyl sulphurane, $\text{Et}\cdot\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot\text{C}_2\text{H}_5$, is heated for many hours with excess of ethyl iodide at 100° and the product extracted with water, a crystalline compound is obtained which is either diethylvinylsulphurane or triethylsulphine iodide, whilst the portion insoluble in water yields ethylene bisulphide on fractional distillation.

The diethyl-derivative of ethylene mercaptan, $\text{Et}\cdot\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot\text{Et}$, when treated with ethyl iodide in like manner, is converted into a mixture of triethylsulphine iodide and ethylene bisulphide.

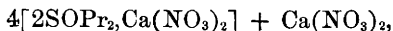
W. P. W.

Propane-derivatives. By C. WINSSINGER (*Bull. Soc. Chim.*, **48**, 108—112).—The product of the action of bromine on excess of propyl alcohol contains an alcohol which boils constantly at 87° , but has all the other properties of propyl alcohol. After dehydration by means of potassium carbonate, it boils at 92° . It is evident that a hydrate of primary propyl alcohol does actually exist.

Propyl mercaptan and propyl sulphide boil at $67\text{--}68^\circ$ and $141\cdot5\text{--}142\cdot5^\circ$ respectively, under a pressure of 772 mm. Cahours's number, 130—135°, for the boiling point of propyl sulphide was doubtless due to the presence of impurities, one of which was most probably the mercaptan formed in consequence of the partial decomposition of the potassium sulphide into hydrosulphide during the preparation of the derivative. This decomposition becomes much more marked with the higher members in the series.

Orthopropylsulphonic acid is obtained by the action of nitric acid of sp. gr. 1·3 on propyl mercaptan. The reaction is violent, and the first products are nitrogen oxides and a red oil, probably ethyl thioethylsulphonate, which gradually dissolves as the effervescence ceases.

Orthopropyl oxysulphide is obtained by the action of nitric acid of sp. gr. 1·2 on propyl sulphide. It forms long, colourless, and odourless needles, which melt at $14\cdot5\text{--}15^\circ$, cannot be distilled without decomposition, and dissolve in water, alcohol, and ether. It burns with a brilliant flame, and is easily reduced by ferrous chloride or by nascent hydrogen. When a solution of the oxysulphide and calcium nitrate is concentrated, it yields a fibrocrySTALLINE compound,



which melts at 80° , and shows the phenomena of supersaturation and superfusion in a very marked manner.

To obtain *diorthopropyl sulphone*, it is necessary to use a warm concentrated solution of potassium permanganate as the oxidising agent. The sulphone crystallises in beautiful, transparent scales, soluble in water, but more soluble in alcohol and ether. It cannot be distilled without decomposition otherwise than in a current of steam.

Monopropylphosphoric acid is contained in the dense viscous residue obtained in the preparation of propyl chloride by the action of phosphorus pentachloride on propyl alcohol. This residue also contains an

acid, which yields a barium salt of the composition $\text{PO}(\text{OPr})\text{O}_2\text{Ba}$, anhydrous at 100° , and soluble in cold water, from which it separates on boiling, and an ethereal salt, $\text{PO}(\text{OPr})_3$, which is most soluble in water at 70 – 80° , dissolves in alcohol and ether, and cannot be distilled without decomposition, even in a vacuum. C. H. B.

Synthesis of Diethyl Methyl Carbinol. By A. REFORMATSKY (*J. pr. Chem.* [2], **36**, 340–347).—Diethyl methyl carbinol, CMeEt_2OH , is prepared by the action of zinc on a mixture of diethyl ketone (100 grams) and methyl iodide (495 grams), and subsequent treatment with water. It is a colourless, mobile liquid, having a pleasant smell resembling trimethyl carbinol, boils at 122 – 123° , and has the sp. gr. 0.8237 at 20° , 0.8194 at 25° , 0.8179 at 30° , and 0.8143 35° (water at $0^\circ = 1$). The acetate is a colourless liquid, boiling at 148° (corr.). The iodide boils at 140 – 144° , and is partly decomposed on distillation. When oxidised with chromic mixture, diethyl methyl carbinol yields acetic acid as the sole product. G. T. M.

Bromination of Allyl Alcohol. By I. FINK (*Monatsh.*, **8**, 561–562).—By bromination of allyl alcohol in absence of water, a dibromhydrin is formed almost in the theoretical proportions, as observed by Markownikoff and v. Tollens. In the presence of water, there is formed in addition a monobromhydrin, $\text{C}_3\text{H}_7\text{BrO}_2$, boiling at 138° , at a pressure of 17 mm.; it is shown to be of this constitution by its conversion into glycerol and triacetin. V. H. V.

Diisobutenyl Oxide. By S. PRZYBYTEK (*Ber.*, **20**, 3239–3246).—The methods of preparation of the following substances have already been given (this vol., p. 123). The dichlorhydrin, $\text{C}_8\text{H}_{14}\text{Cl}_2(\text{OH})_2$, is a thick, viscid, pale-yellow liquid, of faint odour and burning taste.

Diisobutenyl oxide, $\text{CMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe}$ with CH_2 and CH_2 groups in brackets and O below each, is a colourless, mobile liquid, of agreeable odour and burning taste; it is heavier than water, and boils at 170 – 180° under 125 mm. pressure. As was to be expected from their respective constitutions, it combines with water with greater slowness and difficulty than does erythrene dioxide.

Octylerythrol, $\text{C}_8\text{H}_{14}(\text{OH})_4$, is a thick and very viscid liquid, of bitter taste, readily soluble in water and alcohol, but insoluble in ether. It can be formed directly from the chlorhydrin by heating with potash and a large excess of water. A. J. G.

Action of Hydrogen Chloride on Glycerol. By A. FAUCONNIER and J. SANSON (*Bull. Soc. Chim.*, **48**, 236–238).—Dry hydrogen chloride was passed into glycerol for five days, in an apparatus provided with a reflux condenser. The fraction of the product boiling below 80° contains hydrochloric acid and water, together with a small quantity of an oily substance precipitated by water; the fraction 80 – 120° contains the two dichlorhydrins, in quantity equal to half the weight of the glycerol; the fraction 120 – 150° contains glyceryl monochlorhydrin, and substances which crystallise in the receiver. The products boiling above 150° have not yet been examined.

The crystalline solid in the last fraction amounts to 0.75 per cent. of the glycerol used. It crystallises from alcohol in white needles, which have the same composition as epichlorhydrin, and melt at 109—110°. The substance is probably a polymeride of epichlorhydrin; it dissolves readily in cold benzene, ether, carbon bisulphide, and chloroform, is somewhat soluble in alcohol, especially on heating, and dissolves slowly in boiling water, from which it crystallises in very long needles.

C. H. B.

Sugar-like Nature of Formose. By O. LOEW (*Ber.*, **20**, 3039—3043).—A solution of formose (10 grams) in 1 litre of water is boiled in a reflux apparatus, and the whole extracted with chloroform; the residue obtained by evaporating the chloroform is treated with alcohol, aniline, and a little hydrochloric acid, when an intense red coloration is produced, showing the presence of furfuraldehyde. When formose is digested with 1 per cent. sulphuric acid on a water-bath, more furfuraldehyde is obtained than from other sugars.

Formose has all the following characteristics of sugar:—(1) Sweet taste; (2) strong reducing power; (3) ready decomposition by dilute alkali; (4) formation of saccharic acid by the action of lime; (5) power of combination with hydrogen and hydrogen cyanide, and formation of an osazone; (6) formation of humous substances by acids; (7) formation of furfuraldehyde by dilute acid; (8) capability of fermentation. The author concludes with a criticism of Wehmer's paper on the carbohydrate nature of formose (this vol., p. 40).

N. H. M.

Erythrene Dioxide. By S. PRZYBYTEK (*Ber.*, **20**, 3234—3239).—Erythrene dioxide, when treated with bromine in tubes immersed in cold water, is gradually converted into a citron-yellow, crystalline dibromide, which is insoluble in water, alcohol, and chloroform, and readily decomposes with evolution of hydrogen bromide.

A polymeride of the dioxide is obtained in very small quantities by heating the dioxide at 110—130° (below its boiling point = 137°), a better yield being obtained at 140—150°, but the best yield is obtained when sealed tubes containing powdered anhydrous sodium sulphate just moistened with the dioxide are heated at 110—120° for 10 days. In all cases the polymerisation is very incomplete. It is an amorphous, colourless substance, devoid of taste and odour, and insoluble in water, alcohol, ether, benzene, and chloroform. It can, although with difficulty, be converted into erythrol and its derivatives.

Dihydroxyerythrenedisulphonic acid, $C_4H_6(OH)_2(SO_3H)_2$, is obtained when erythrene dioxide is shaken with a slight excess of concentrated aqueous hydrogen sodium sulphite, and the sodium salt formed decomposed with oxalic acid. It forms a deliquescent mass of felted needles, and is very unstable, charring when gently heated, and yielding sulphurous anhydride when its aqueous solution is heated at 50°. Its salts, on the contrary, are very stable.

A. J. G.

Inosite. By LOBIN (*Bull. Soc. Chim.*, **48**, 235—237).—The author showed 10 years ago, from its behaviour with oxalic acid, that inosite is a polyhydric alcohol (*Abstr.*, 1878, 398).

C. H. B.

Carbohydrates. By Å. G. EKSTRAND and C. J. JOHANSON (*Ber.*, **20**, 3310—3317).—The authors have obtained a new carbohydrate from the haulm of the *Phleum pratense*. The haulm is thickened at its lower end to a bulb and in the autumn this bulb increases in size and becomes filled with a concentrated solution of a carbohydrate to which the authors give the name *graminin*. This substance is a powder resembling starch, of the formula $6C_6H_{10}O_5 + H_2O$, and fuses with decomposition at 215° . It is soluble in water and in caustic potash, insoluble in alcohol. From its aqueous solutions, baryta-water throws down a precipitate which redissolves in excess of the precipitant. It does not give a blue coloration with iodine: it reduces silver nitrate, but not Fehling's solution. Under the microscope, graminin shows spheroidal granules which are sometimes concentrically striated: on the addition of water a part dissolves, but the larger part remains in the form of half-spheres which show radial striæ. The authors have also obtained graminin from the rhizome of *Baldingera arundinacea*, but in this case a part of the carbohydrate occurs in a less soluble modification. This latter modification shows decided cruciform or semi-circular striæ in polarised light. Graminin also seems to be present in the rhizomes of *Calamagrostis agrostis* and of *Teisetum hierochloa*. This carbohydrate seems closely related to inulin and irisin, as is apparent from the following comparison of their properties:—

	Solubility in 100 parts H_2O at ordinary temp.	Rotatory power. $[\alpha]_D$.	Melting point.
Graminin { sol. variety..	3.29 parts	— 48.12°	215°
{ insol. „ ..	1.79 „	— 49.27	205
Irisin	3.26 „	— 52.34	160
Inulin	0.96 „	— 34.53	160

From *Dracaena australis* the author has obtained a carbohydrate, $6C_6H_{10}O_5 + H_2O$, which very closely resembles tritacin from *Triticum repens*. It differs, however, from the latter in its rotatory power, which is $[\alpha]_D = -36.61^\circ$, whilst that for tritacin, is $[\alpha]_D = -41.07^\circ$.

L. T. T.

Inulin. By M. HÖNIG and S. SCHUBERT (*Monatsh.*, **8**, 529—560).—Braconnot, Berzelius, and Payen have observed the formation of certain dextrans and saccharine substances when inulin is heated; whilst Dragendorff has described intermediate products between inulin and lævulose formed by heating inulin with water under pressure. In this paper, a long account is given of experiments on the saccharification of inulin, effected either by heating inulin in glycerol or with dilute mineral acids: the specific rotatory and cupric oxide reducing powers of the various intermediate products are also set forth in a series of tables. The principal results obtained are as follows:—(1.) The intermediate products obtained by heating inulin with dilute mineral acids, so far as they are directly comparable, seem to be identical with the products obtained by heating inulin by itself. (2.) These dextrin-like substances differ from one another by their specific rotatory power, as also by their solubility in water and alcohol, and their precipitability by barium hydrate. At a lower

temperature, the substances formed more nearly resemble inulin as regards their sparing solubility, whilst at a higher temperature, at first certain products, *metinulin* and *inuloid* are produced, which are readily soluble in water, and not precipitated by barium hydrate. After a more profound change, the substance formed shows successively a slight lævorotatory, then no rotatory power, and finally a dextrorotatory power. The specific rotatory power varies from $[\alpha]_D = -41.5$, that of inulin, to $[\alpha]_D = +30.68$, that of the final dextrin. (3.) The substances without specific rotatory power are not identical with lævuloses. (4.) The saccharification of inulin is effected rapidly by dilute acids, reaching its maximum in 15 to 30 minutes, according to the concentration; lævulose and the above-mentioned dextrins are simultaneously produced.

The authors have also succeeded in obtaining lævulose in crystals sufficiently well developed for measurement, by frequently recrystallising the crude crystalline lævulose from absolute alcohol, the crystallisation in each case being induced by dropping in a solid crystal; a similar product was also obtained by the saccharification of inulin. Lævulose crystallises in the rhombic system, individual crystals being of the prismatic and combined crystals of the octohedral type. The axial ratio is $a : b : c = 0.80067 : 1 : 0.90674$, whilst $110 : \bar{1}\bar{1}0 = 77^\circ 22'$ and $011 : 0\bar{1}\bar{1} = 84^\circ 24'$. The crystals are slightly biaxial, resembling, as regards their action on polarised light, certain mixtures of sodium-ammonium and potassium-sodium tartrates. The specific rotatory power of an aqueous solution of the pure lævulose was $[\alpha]_D = -89.74$, $L = 200$ mm., $c = 3.6555$; $t = 22^\circ$. This value when calculated by means of the factor 1.129 gives for $[\alpha]_D$ the value -87.84° . Analyses are also given of the pure product, which prove that the formula $C_6H_{12}O_6$ expresses the composition of lævulose.

V. H. V.

Fermentation of Glyceraldehyde. By E. GRIMAUX (*Compt. rend.*, 105, 1175—1177).—By oxidising glycerol by means of platinum-black, the author had previously obtained a liquid which seemed to contain glyceraldehyde, although the latter could not be isolated (*Abstr.*, 1887, 695). When this product is distilled in a vacuum with dilute hydrochloric acid, its rotatory power is considerably reduced, and a gummy residue is left which is soluble in absolute alcohol. The residue therefore contains no dextrin, and since dextrose is converted into dextrin under these conditions, it follows that the product of the action of platinum-black on glycerol contains no dextrose. With phenylhydrazine, it yields a compound identical with the hydrazine-derivative obtained by Fischer and Tafel from the products of the oxidation of glycerol by nitric acid. The author oxidised glycerol by Fischer and Tafel's process, neutralised with potassium hydroxide, extracted with alcohol, and evaporated the solution to dryness in a vacuum. The product thus obtained has very little reducing power, but if boiled with very dilute sulphuric acid it recovers its reducing power, and after neutralisation it ferments readily in contact with yeast. Glyceraldehyde is not converted into glucose by treatment with hydrochloric acid.

This is the first instance of the synthetical formation of a sugar which undergoes alcoholic fermentation. It is evident that the property of fermenting in this manner is not confined to carbohydrates containing C_6 and C_{12} .

C. H. B.

Decomposition of Nitrosoketones. By H. v. PECHMANN (*Ber.*, **20**, 3213—3214; compare this vol., p. 146).—When boiled with dilute sulphuric acid, fatty nitroketones are converted into hydroxylamine and diketones. When the liquid obtained by treating an alkaline solution of ethyl methylacetoacetate with sodium nitrite and sulphuric acid is distilled with much sulphuric acid, a yellow distillate containing diacetyl is obtained.

N. H. M.

Action of Zinc Ethide and Zinc Iodoethide on Dipropylketone. By P. MENSCHIKOFF (*J. pr. Chem.* [2], **36**, 347—352).—Both zinc ethide and zinc iodoethide form condensation-products with dipropyl ketone, but only the compound of the iodoethide yields a tertiary alcohol on treatment with water.

G. T. M.

Diacetyl and its Homologues. By H. v. PECHMANN (*Ber.*, **20**, 3162—3164).—By successive treatment with sodium hydrogen sulphite and dilute acids, the homologues of nitrosoacetone are converted into α -diketones (homologues of diacetyl), ammonia and sulphuric acid being also produced. From nitrosomethylacetone, *diacetyl* is obtained: $\text{COMe} \cdot \text{CMe} \cdot \text{NOH} + \text{H}_2\text{SO}_3 = \text{COMe} \cdot \text{CMe} \cdot \text{NSO}_3\text{H} + \text{H}_2\text{O} = \text{COMe} \cdot \text{COMe} + \text{NH}_4\text{HSO}_4$.

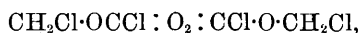
It is a yellowish-green oil which boils without decomposition at 87 — 88° , and does not solidify when placed in a freezing mixture of ice and salt; its odour resembles that of acetone, and its vapour is the colour of chlorine; it dissolves in 4 parts of water at 15° , forming a yellow solution, and is miscible with ordinary solvents. It is decomposed by alkalis or hot alkaline carbonates, forms a colourless, crystalline substance with ammonia, and with phenylhydrazine yields two hydrazides, melting at 133° and 242° respectively. With aniline, it forms a crystalline product; with orthodiamines, liquid quinoxalines are produced, and it combines readily with alkaline hydrogen sulphites. When reduced in acid solution, it is converted into a benzoïu which reduces Fehling's solution instantly at the ordinary temperature. Since in its physical properties diacetyl differs so considerably from glyoxal, the latter compound must be considered as a polymeric di-formyl: diacetyl, however, resembles its higher homologues dibutyl and diisovaleryl.

F. S. K.

Chlorinated Methyl Formates. By W. HENTSCHEL (*J. pr. Chem.* [2], **36**, 305—317; compare *Abstr.*, 1887, 1027, 1099).—Trichloromethyl chloroformate, $\text{COCl} \cdot \text{OCCl}_3$, is obtained among other products of the chlorination of methyl chloroformate. When heated at 300° , it decomposes into twice its volume of carbonyl chloride; at a dull-red heat, it yields carbonic anhydride and carbon tetrachloride, whilst in presence of aluminium chloride it is rapidly and completely

resolved into these substances, giving almost a theoretical yield of carbon tetrachloride. Both dry and aqueous ammonia convert it into carbamide, but, contrary to the statement of Cahours, no trichloracetamide is formed. If aniline is used instead of ammonia, diphenylcarbamide is formed which, on further treatment with trichloromethyl chloroformate, yields phenyl isocyanate. Trichloromethyl chloroformate does not react with benzene when heated in closed tubes at 150°, but if the substances are brought together in presence of aluminium chloride, triphenylchloromethane is produced. With alcohol and phenol, trichloromethyl chloroformate yields trichloromethyl carbonate, $\text{OMe}\cdot\text{CO}\cdot\text{OCCl}_3$, and phenyl chloroformate, $\text{COCl}\cdot\text{OPh}$, respectively, whilst it is practically without action on unsaturated hydrocarbons, such as ethylene and amylenes, when heated with them in sealed tubes. G. T. M.

Chlorinated Methyl Formates. By W. HENTSCHEL (*J. pr. Chem.* [2], **36**, 468—480).—Trichloromethyl dichloroformate, $\text{C}_4\text{H}_3\text{Cl}_5\text{O}_4$ (Abstr., 1887, 1028), is not formed by heating together methyl chloroformate and perchloromethyl formate. By the action of aluminium chloride, the formate is split up into carbonic anhydride, methylene chloride, and chloroform, pointing to the formula



rather than to $\text{OMe}\cdot\text{C}_2\text{O}_2\text{Cl}_2\cdot\text{O}\cdot\text{CCl}_3$, where chloromethane and tetrachloromethane should be the products.

By distilling the formate (1 mol.) with anhydrous sodium acetate (5 mols.), acetic acid, acetic anhydride, methylene diacetate, and carbonic oxide and anhydride are obtained; if a smaller proportion of sodium acetate is used, acetic chloride and methylene diacetate are formed. The action of aluminium chloride on the formate dissolved in benzene yields di- and tri-phenylmethane. Aniline acts on the formate, producing a crystalline substance, $\text{C}_4\text{H}_3\text{Cl}_3\text{O}_4(\text{NHPh})_2$, of unpleasant odour, melting at 45°. By the action of sodium phenoxide on the formate, a phenyl ether corresponding with this anilide was obtained.

On chlorinating methyl chloroformate, a heavy oil, either $\text{C}_8\text{H}_9\text{Cl}_7\text{O}_8$ or $\text{C}_6\text{H}_7\text{Cl}_5\text{O}_6$, boiling at 180°, is obtained. Its vapour-density could not be ascertained. A. G. B.

Action of Triethylamine on α -Bromobutyric Acid. By E. DUVILLIER (*Bull. Soc. Chim.*, **48**, 3—6).—When a solution of α -bromobutyric acid (1 mol.) is added to a saturated aqueous solution of triethylamine (2—3 mols.), there is some development of heat, and the liquid separates into two layers, the upper of which is unaltered triethylamine. The mixture is heated to complete the reaction, and the excess of triethylamine distilled off. The products are triethylamine hydrobromide and α -hydroxybutyric acid, the latter being soluble in ether. The barium salt of this acid is almost insoluble in alcohol. The zinc salt crystallises with 2 mols. H_2O in small nodules, which lose their water at 110°. It is almost insoluble

in alcohol. No betaine is formed in this reaction, and hence the behaviour of triethylamine is analogous to that of potassium, barium, or silver hydroxide.

When the dry substances are mixed in the same proportions, there is likewise some development of heat, and the reaction is completed by heating in closed vessels. The products are α -hydroxybutyric acid, traces of crotonic acid, and tetrethylammonium bromide.

C. H. B.

Solubility of Salts of Isovaleric, Methylenebutyric, and Isobutyric Acids. By L. SEDLITZKY (*Monatsh.*, **8**, 563—576).—In this paper determinations are given of the solubility of various salts of isovaleric, methylenebutyric, and isobutyric acids, by the method of heating and cooling described by Raupenstrauch; from these determinations, formulæ are deduced, and the calculated results in each case are compared with those found. These formulæ are given below:—

$$\text{Silver isovalerate, } S = 0.1774 + 0.003349(t - 0.2) + 0.000006528(t - 0.2)^2.$$

$$\text{Calcium isovalerate, } S = 18.429 + 0.10514(t - 0.2) - 0.001091(t - 0.2)^2.$$

$$\text{Calcium isobutyrate, } S = 20.383 + 0.08061(t - 1) + 0.0006522(t - 1)^2.$$

$$\text{Silver methylenebutyrate, } S = 1.1116 + 0.0002978(t - 1) + 0.0002105(t - 1)^2.$$

$$\text{Calcium methylenebutyrate, } S = 28.9822 + 0.33186(t - 0.6) + 0.004417(t - 0.6)^2.$$

Barium methylenebutyrate could not be obtained in a crystalline form. The curves of solubility in terms of degrees are given in a series of diagrams.

V. H. V.

Oxidation of Palmitic Acid. By M. GRÖGER (*Monatsh.*, **8**, 484—497).—An account is given of experiments on the oxidation of palmitic acid with alkaline permanganate, under various conditions of concentration. The principal products formed are acids of the oxalic series, namely, oxalic, succinic, and adipic; acids of the acetic series, namely, acetic, butyric, caproic, and probably caprylic; and acids of the lactic series, namely, hydroxyvaleric and dihydroxypalmitic acids. Other conditions remaining the same, acids of lower molecular weight are produced with greater concentration of the oxidising solution, and acids of higher molecular weight with more dilute solutions. The conditions of each experiment, the products obtained, and the methods by which they were separated, are discussed in detail in the paper.

V. H. V.

Mixed Acid Anhydrides. By W. AUTENRIETH (*Ber.*, **20**, 3187—3191).—The general method for preparing the mixed anhydrides consists in heating the acid with two or three times the calculated amount of acetic anhydride in a reflux apparatus for $\frac{1}{4}$ to $\frac{1}{2}$ an hour. The product is treated with sodium carbonate to remove excess of

acetic anhydride as well as the acetic acid; the anhydride separates as an oil from the alkaline liquid.

Acetocaproic anhydride, $C_6H_{11}O \cdot OAc$, is a colourless liquid, which is lighter than water and boils at $165-175^\circ$.

Acetovaleric anhydride, $C_6H_9O \cdot OAc$, resembles the above compound; it boils at $147-160^\circ$.

Aceto- β -thioethylcrotonic anhydride, $SEt \cdot CMe \cdot CH \cdot CO \cdot OAc$, is a thick yellowish-brown oil, heavier than water, which when exposed to air, gradually decomposes with separation of crystals of thioethylcrotonic acid. It gives a dark-red coloration with sulphuric acid, but does not show the dark-green coloration characteristic of the thioethylcrotonic acids when treated with isatin and sulphuric acid. Nitric acid acts violently on it.

Acetobenzoic anhydride, $COPh \cdot OAc$ (Gerhardt, *Annalen*, **87**, 85), is readily obtained by boiling benzoic acid with acetic anhydride. When treated with ammonia, it is converted, with development of heat, into benzamide and ammonium acetate.

Valerylphenylhydrazide, $NHPh \cdot NH \cdot C_5H_9O$, prepared by mixing acetovaleric anhydride with phenylhydrazine, crystallises in yellowish-white plates melting at 101° ; it dissolves readily in alcohol, ether, and chloroform, sparingly in light petroleum.

Capronyl phenylhydrazide, $NHPh \cdot NH \cdot C_6H_{11}O$, crystallises from light petroleum in white needles melting at $116-117^\circ$ (compare Abstr., 1887, 797).

N. H. M.

Oxidation-products of the α -Hydroxy-acids of the Fatty Series. By V. ARISTOFF and N. DEMJANOFF (*Chem. Centr.*, 1887, 1157, from *J. Russ. Chem. Soc.*, 1887, 257-271).—The authors studied the intermediate products which are obtained by oxidising the ethereal salts of the α -hydroxy-acids, on the assumption that the ethereal salts of the ketonic acids formed by that reaction ought to show a greater stability than the ketonic acids themselves. Potassium permanganate was used as the oxidising agent. Ethyl lactate, in sulphuric acid solution, gave ethyl pyruvate. Ethyl hydroxybutyrate gave about 15 per cent. of the theoretical yield of ethyl propionyl-formate, $CH_3 \cdot CH_2 \cdot CO \cdot CO_2C_2H_5$. It is thus shown that in oxidising the α -hydroxy-acids, α -ketonic acids are formed as intermediate products.

J. W. L.

Lactones and Lactonic Acids. By R. FITTIG (*Ber.*, **20**, 3179-3185).—When the lactonic acids, $CHX \langle \begin{smallmatrix} CH(COOH) \\ -O \cdot CO \cdot CH_2- \end{smallmatrix} \rangle$, obtained by the union of aldehydes with succinic acid, are boiled, a part distils unchanged, but the greater portion decomposes yielding, as chief products, the monobasic unsaturated acids, $CHX \cdot CH \cdot CH_2 \cdot COOH$, together with the lactones $CHX \langle \begin{smallmatrix} CH \cdot CH_2 \\ -O \cdot CO- \end{smallmatrix} \rangle$, and a small quantity of the anhydride of the bibasic acids, $COOH \cdot CHX \cdot CH_2 \cdot COOH$ (?).

Propylparaconic acid, $CHPr \langle \begin{smallmatrix} CH(COOH) \\ -O \cdot CO \cdot CH_2- \end{smallmatrix} \rangle$, prepared from butyraldehyde and succinic acid, crystallises well, and melts at 73.5° . It

readily yields *heptylenic acid*, $C_7H_{12}O_2$, boiling at $224-226^\circ$, and heptolactone (Kiliani, Abstr., 1886, 687), $CHPr<\overset{-CH_2}{O.CO}>CH_2$. This boils at $232-237^\circ$ without change, and behaves quite similarly to the other lactones. The abnormal behaviour observed by Kiliani (*loc. cit.*) was probably due to impurity.

Trichloromethylparaconic acid, $CCl_3 \cdot CH<\overset{CH(COOH)}{O.CO-CH_2}>$, obtained by treating chloral with sodium succinate and acetic anhydride, melts at 97° , and is sparingly soluble. When treated with an excess of baryta-water, it is converted into the barium salt of iso-citric acid. The latter has therefore the constitution $COOH \cdot CH(OH) \cdot CH(COOH) \cdot CH_2 \cdot COOH$; it could not be isolated, as the aqueous solution when evaporated yields the lactonic acid $COOH \cdot CH<\overset{CH(COOH)}{CH_2.CO.O}>$. This is crystalline, dissolves in water in all proportions, and gives salts of isocitric acid when treated with bases.

Phenylisohomoparaconic acid, $C_{12}H_{12}O_4$, is obtained together with phenylhomoparaconic acid (Abstr., 1883, 473) by the action of benzaldehyde on methylsuccinic acid; it melts at 124.5° . The two acids react similarly, and when distilled yield phenylbutylenes, unsaturated acids, $C_{11}H_{12}O_2$, and *methylnaphthols*, $C_{10}H_8Me.OH$. The *methylnaphthol* from methylhomoparaconic acid has probably the constitution $[Me : OH = 3 : 4]$; it forms yellow needles melting at 89° . The *naphthol* from the iso-acid is colourless, melts at 92° , and is more stable; the constitution $[Me : OH = 2 : 4]$ is ascribed to it. Both compounds give with bleaching powder a green precipitate, which afterwards becomes yellow. When distilled over heated zinc-dust, they both yield β -methylnaphthalene; this melts at $37-38^\circ$ (not 32.5° , Schulze, Abstr., 1884, 1184), and has an odour resembling that of naphthalene.

When the tetrabromo-derivative of ethyl ketipate (Fittig and Daimler, Abstr., 1887, 361) is treated with ammonia, alcohol, oxamide (1 mol.) and dibromacetamide (2 mols.) are formed. The constitution of ketipic acid is therefore $COOH \cdot CH_2 \cdot CO \cdot CO \cdot CH_2 \cdot COOH$. The reaction is similar to that observed by Hantzsch and Zeckendorf in the case of ethyl tetrachlorodiketo adipate (Abstr., 1887, 727), which can be prepared by the action of chlorine on ethyl ketipate.

Dimethyldiketone (Diacetyl), $COMe \cdot COMe$, is obtained by distilling ketipic acid. It forms a pure yellow liquid boiling at $87-89^\circ$, rather soluble in water, miscible with alcohol and ether. It has an odour resembling that of quinone, and yields a very unstable compound with sulphurous anhydride. The *phenylhydrazine compound*, $C_{16}H_{18}N_4$, crystallises in splendid, slightly yellow needles which melt at 236° with decomposition; it is sparingly soluble in ether, less soluble in alcohol. The *dioxime*, $C_4H_8N_2O_2$, is obtained as a white crystalline precipitate when a dilute solution of the diketone is treated with free hydroxylamine; a very small amount of the diketone can be detected by means of this reaction. The dioxime is very stable, and melts without decomposition at 234° (compare v. Pechmann, this vol., p. 248). N. H. M.

Action of Ammonia on Ethyl Acetoacetate and its Derivatives. By M. CONRAD and W. EPSTEIN (*Ber.*, **20**, 3052—3058).—Methyl “amidoacetoacetate,” $\text{NH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{COOMe}$, is prepared by passing ammonia through a cooled mixture of methyl acetoacetate with ether (2 parts) in presence of powdered ammonium nitrate. It crystallises in lustrous, colourless prisms, a centimetre long, melts at 85° , and sublimes unchanged.

Methyl “amidoethylacetoacetate,” $\text{NH}_2\cdot\text{CMe}\cdot\text{CEt}\cdot\text{COOMe}$, is prepared by treating 11.6 grams of methyl acetoacetate with 2.3 grams of sodium and 25 grams of methyl alcohol, and adding ethyl iodide; the whole is afterwards heated on a water-bath; the methyl ethylacetoacetate so obtained boils at $186\text{--}188^\circ$. This is treated with ammonia, and the crystalline product crystallised from alcohol. It melts at $36\text{--}37^\circ$.

Ethyl “amidomethylacetoacetate,” $\text{NH}_2\cdot\text{CMe}\cdot\text{CMe}\cdot\text{COOEt}$, is prepared by the action of sodium, in the form of wire, on ethyl β -amidocrotonate (m. p. 37°) dissolved in ether, the sodium compound being then warmed with methyl iodide. It is a white, crystalline substance readily soluble in ether, alcohol, and light petroleum; it melts at 52° , sublimes readily, and has a sharp odour and taste. Boiling hydrochloric acid decomposes it very readily into ammonium chloride and ethyl methylacetoacetate.

Ethyl “amidoethylacetoacetate,” $\text{NH}_2\cdot\text{CMe}\cdot\text{CEt}\cdot\text{COOEt}$, is formed by the action of ammonia on ethyl ethylacetoacetate; it was prepared by Geuther. It forms white plates melting at 60° .

Ammonia has no action on ethyl diethylacetoacetate; ethyl “amidoacetoacetate” is therefore probably ethyl amidocrotonate and not an imidobutyrate (compare Kuckert, *Ber.*, **18**, 618). Ethyl dichloroacetoacetate (cooled with ice) is decomposed by ammonia into ethyl-dichloroacetate and acetamide.

Methyl β -amidoethylcrotonate, $\text{NH}_2\cdot\text{CMe}\cdot\text{CMe}\cdot\text{COOMe}$, melts at $58\text{--}59^\circ$.

Ethyl “amidoacetosuccinate,” $\text{NH}_2\cdot\text{CMe}\cdot\text{C}(\text{COOEt})\cdot\text{CH}_2\cdot\text{COOEt}$, crystallises in white, lustrous prisms melting at 72° (compare Brandes, *Jen. Zeitsch.*, **3**, 35).
N. H. M.

Action of Aqueous Ammonia on Alkylated Alkyl Acetoacetates, and of Alcohols on the Carboxylic Alkyl-group in Acetoacetates. By T. PETERS (*Ber.*, **20**, 3318—3324).—Brandes (*Jen. Zeitsch.*, **3**, 35, and *Zeit. für. Chem.*, 1866, 437) described the formation of two compounds, $\text{C}_7\text{H}_{13}\text{O}_2\text{N}$ and $\text{C}_5\text{H}_9\text{O}_2\text{N}$, by the action of aqueous ammonia on methyl ethylacetoacetate. Conrad and Epstein (preceding Abstr.), employing gaseous ammonia, only obtained the compound $\text{C}_7\text{H}_{13}\text{O}_2\text{N}$, or methyl amidoethylcrotonate, $\text{NH}_2\cdot\text{CMe}\cdot\text{CEt}\cdot\text{COOMe}$. The author has repeated Brandes' experiments and, besides $\text{C}_7\text{H}_{13}\text{O}_2\text{N}$, obtained ethylacetoacetamide, $\text{CH}_3\cdot\text{CO}\cdot\text{CHEt}\cdot\text{CONH}_2$ (m. p. 96°). This is undoubtedly the compound described by Brandes as $\text{C}_5\text{H}_9\text{O}_2\text{N}$, and probably obtained by him in an impure state. Ethylic methyl-, isobutyl- and isoamyl-acetoacetates similarly yielded methyl-, isobutyl-, and isoamyl-acetoacetamides, melting respectively at 73° , 85° , and 127° , whilst, if Brandes' supposition is correct that in his experiments the

substituted ethyl-group was eliminated, the above three compounds must have yielded amides which were identical.

In preparing methyl ethylacetoacetate the author found that if ethyl alcohol was employed as the solvent, the larger quantity of the methyl salt was converted into the ethyl salt. Making further experiments, he found that isobutyl or isoamyl salts could be readily obtained by the action of the respective alcohol on the ethyl salts, the action taking place especially easily in the presence of a small quantity of sodium. He was similarly able to convert ethyl ethylacetoacetate into the methyl salt in the presence of sodium, but the action was less complete than when replacing a lower by a higher alkyl-group.

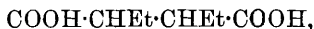
L. T. T.

Isomeric Dialkylsuccinic Acids. By C. A. BISCHOFF (*Ber.*, 20, 2988—2992).—The author, in conjunction with Voit, has saponified ethyl α - β -dimethylethenyltricarboxylate on the large scale, and has confirmed the results previously obtained by him in conjunction with Rach (*Abstr.*, 1885, 885). In addition, a second acid is also formed which melts at 120°, and is identical with the readily soluble butanedicarboxylic acid (*Abstr.*, 1887, 45), and the product of change from the sparingly soluble dimethylsuccinic acid of high melting points. Voit has also succeeded in converting the two isomeric dimethylsuccinic acids into pyrocinchonic acid.

Two symmetrical diethylsuccinic acids are obtained by saponifying either ethyl diethylacetylenetetetracarboxylate or the compound $\text{CEt}(\text{COOEt})_2\cdot\text{CHEt}\cdot\text{COOEt}$; one of the acids is sparingly soluble, melts at 189°, and can be converted into the second, which is readily soluble, and melts at 127—128°. These acids are probably identical with Hell and Mühlhäuser's isosuberic acids (*Abstr.*, 1880, 542). Experiments are in progress with the object of splitting into two optically active compounds the optically inactive diethylsuccinic acid corresponding with racemic acid.

W. P. W.

Symmetrical Diethylsuccinic Acids. By E. HJELT (*Ber.*, 20, 3078—3080).—Symmetrical diethylsuccinic acid,



is prepared by the action of ethyl α -bromobutyrate on ethyl malonate and sodium ethoxide. The ethyl ethylbutenyltricarboxylate so obtained, which boils at 280—282°, is saponified, and the acid (m. p. 147°) heated at 150°. The residue is then crystallised from hot water, when two acids of the same composition are obtained; the one melts at 189—190°, and is identical with that prepared by Otto by reducing xeronic acid (*Annalen*, 239, 279), and gives an ethyl salt boiling at 233°, which is identical with that obtained by Hell (*Ber.*, 6, 30) by the action of silver on ethyl α -iodobutyrate. The second acid melts at 127°. When the acid melting at 189—190° is heated, it is converted into an anhydride which boils at about 240°; when this is boiled with water, it yields the acid melting at 127°. 100 parts of water at 23° dissolve 0.61 part of the acid of higher melting point, and about 2.4 parts of the lower melting acid. The two acids differ also in crystalline form (compare Otto and Rössing, this vol., p. 45).

N. H. M.

Action of Ammonia on Alkyl Salts of Fatty Acids. By S. RUHEMANN (*Ber.*, **20**, 3366—3371; compare *Trans.*, 1887, 403).—Phenylhydrazine reacts with ethyl diacetyltartrate, acetylphenylhydrazine being formed. When ethyl diacetyltartaric acid is treated with ammonia, tartramide, $C_4H_8N_2O_4$, is formed. In a similar manner, mucamide is obtained from ethyl tetracetylmucate.

Ethyl aconitate boils at $174\text{--}175^\circ$ under about 22 mm. pressure. When left in contact with aqueous ammonia for 2 to 3 days, it is converted into citrazinamide (*loc. cit.*).

When bromine is added to a solution of citrazinamide in strong hydrochloric acid, the compound $C_6H_3Br_3N_2O_3$ separates as a yellow crystalline precipitate. This is stable when dry, but decomposes slowly in presence of moisture; hot water decomposes it with evolution of carbonic anhydride. It dissolves very readily in ammonia and in aqueous potash. The corresponding *chloro-derivative*, $C_6H_3Cl_3N_2O_3$, resembles the bromine compound, but is more stable; it can be crystallised from water, but the solution decomposes when boiled for some time. Both halogen-derivatives react with aniline, orthotoluidine, and piperidine.

N. H. M.

Apparatus for Distilling Zinc Methyl and Zinc Ethyl. By A. KAULFUSS (*Ber.*, **20**, 3104—3105).—The apparatus, of which a sketch is given, is so constructed that the distillation can be conducted in an atmosphere of carbonic anhydride.

N. H. M.

Disulphones, $R'R'_2(SO_2)_2$ and $R''_2(SO_2)_2$. By R. OTTO and R. C. CASANOVA (*J. pr. Chem.* [2], **36**, 433—451; compare *Abstr.*, 1885, 261 and 537).—*Ethylenediethyldisulphone*, $C_2H_4(SO_2Et)_2$, is prepared by heating an alcoholic solution of sodium ethylsulphinat (2 mols.) with ethylene dibromide (1 mol.); or by heating an alcoholic solution of sodium ethylenedisulphinat (1 mol.) with ethyl bromide (2 mols.). The identity of the products of these two reactions tends to show that the sulphur in these sulphinic acids is hexavalent. The sulphone crystallises in colourless needles, and melts at $136\text{--}137^\circ$. Nascent hydrogen in alkaline solution converts it into sodium ethylsulphinat and alcohol. When heated with aqueous potassium hydroxide, it yields a thick oil, which, with benzoic chloride, gives ethylsulphone-ethyl benzoate, $SO_2Et \cdot CH_2 \cdot CH_2 \cdot OBz$, melting at 118° ; the corresponding alcohol could not be isolated.

Ethylenedimethyldisulphone, $C_2H_4(SO_2Me)_2$, is formed when methyl bromide is substituted for ethyl bromide in the above reaction; it crystallises in pearly scales, melts at 190° , and is soluble in hot water.

Ethylenedipropyldisulphone, $C_2H_4(SO_2Pr)_2$, forms crystals with a pearly lustre, melting at 155° .

Diethylenedisulphone, $C_2H_4 \begin{smallmatrix} SO_2 \\ < \\ SO_2 \end{smallmatrix} C_2H_4$, prepared by the action of sodium ethylenedisulphinat on ethylene dibromide, is identical with the oxidation product of diethylene disulphide.

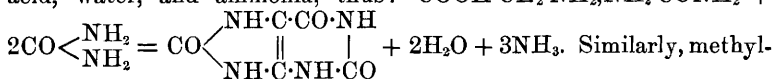
Metaphenylenediethyldisulphone, $C_6H_4(SO_2Et)_2$, prepared by the

action of potassium benzenedisulphinate on ethyl bromide, forms colourless tables melting at 142° .

Phenylene-ethylenedisulphone, $\text{C}_6\text{H}_4\langle\text{SO}_2\rangle\text{C}_2\text{H}_4$, obtained by heating ethylene dibromide with potassium metabenzenedisulphinate, forms very small crystals, insoluble in most solvents. A. G. B.

Synthetical Researches on and Constitution of Uric Acid.

By J. HORBACZEWSKI (*Monatsh.*, **8**, 584—593).—The author has shown that uric acid may be synthetically produced from trichlorolactamide and carbamide; it is also formed, although in smaller quantity, from trichlorolactic acid, as also from amidoacetic acid and carbamide. This last change doubtless depends on the intermediate formation of a glycocine-carbamide which reacts with the carbamide to form uric acid, water, and ammonia, thus: $\text{COOH}\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{NH}_2\cdot\text{CONH}_2 +$

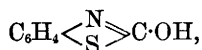


uric acid may be obtained from sarcosine and carbamide, as also from methylhydantoïn and biuret or amyl allophanate. The formation of uric acid from trichlorolactic acid shows that uric acid is an ureide of acrylic acid, whilst the formation of methyluric acid from methylhydantoïn shows that it is a hydantoïn cyanate. The relation of uric acid to lactic acid is of especial physiological importance, as Minkowski has shown that on removal of the liver from geese, considerable quantities of ammonia and lactic acid occur in the urine, whilst the proportion of uric acid is diminished. It has further been shown by Kanëra and the author that in the human organism the proportion of uric acid is increased by doses of glycerol. On the other hand the synthesis of uric acid from amidoacetic acid is of interest, as v. Knierem has proved that in the organism of birds amidoacetic acid (glycocine) is converted into uric acid and expelled as such in the urine; the same phenomenon has also been observed, to a less degree, in the human organism, since the glycocine is for the most part converted into carbamide. V. H. V.

Furfuracrylic Acid. By H. B. HILL (*Ber.*, **20**, 3359)—Bromine acts on furfuracrylic acid with formation of a crystalline compound, $\text{C}_7\text{H}_5\text{Br}_3\text{O}_3$, which is decomposed by water into dibromofurfurethylene and carbonic anhydride. From the dibromo-compound, monobromofurfuracrylic acid crystallising in long needles, and dibromofurfuracrylic acid can be readily prepared. (Compare Markwald, this vol., p. 135.) N. H. M.

Thiazole Compounds. By A. HANTZSCH and J. H. WEBER (*Ber.*, **20**, 3118—3132, and 3336—3337).—Thiazole is the name given to the isomeric compounds, $\langle\begin{smallmatrix} \text{N} : \text{CH} \\ \text{CH} : \text{CH} \end{smallmatrix}\rangle\text{S}$ and $\langle\begin{smallmatrix} \text{CH} : \text{N} \\ \text{CH} : \text{CH} \end{smallmatrix}\rangle\text{S}$; no simple thiazole-derivative is known, but by the condensation of

certain ortho-benzene-derivatives benzene-thiazoles are formed; for instance, hydroxyphenylthiocyanate gives the compound



and all thiocyanic compounds of ketonic or aldehydic nature in which the carbonyl radicle is in the ortho-position to the thiocyanic group are, in their stable form, thiazole-derivatives, the atomic complex, $\text{CO}\cdot\text{CH}\cdot\text{S}\cdot\text{CN}$, changing into $\langle\begin{smallmatrix}\text{C}\cdot\text{N} \\ \text{C}\cdot\text{S}\end{smallmatrix}\rangle\text{C}\cdot\text{OH}$. The term *meso-derivative* is suggested for all compounds in which the hydroxyl-group is displaced. From thiocyanacetone, Tscherniac and Norton (Abstr., 1883, 568) obtained a peculiar base, thiocyanopropimine, to which they gave the formula $\text{NH}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{SCN}$; this substance is, however, meso-amidomethylthiazole, $\langle\begin{smallmatrix}\text{N}\cdot\text{C}(\text{NH}_2) \\ \text{CMe}\cdot\text{CH}\end{smallmatrix}\rangle\text{S}$; by neither of Hofmann's reactions can it be proved that this compound is a primary amine, and with nitrous acid it yields only resinous products, but from its behaviour towards methyl iodide only two hydrogen-atoms can be in combination with nitrogen; the study of its acetyl-derivatives and of thiocyanacetone prove the above formula to be correct.

Methylamidomethylthiazole hydriodide, $\text{C}_4\text{NSH}_4\cdot\text{NHMe}\cdot\text{HI}$, is the principal product of the action of methyl iodide on thiocyanopropimine; it crystallises with 1 mol. H_2O , and when treated with potash yields *methylamidomethylthiazole*; this base is a white, very deliquescent, crystalline substance, not very readily soluble in ether. It has a strongly alkaline reaction, and reacts more readily with methyl iodide than the original base, an abnormal ammonium iodide, $\text{C}_{10}\text{H}_{14}\text{S}_2\text{N}_3\text{I}$, and *dimethylamidomethylthiazole hydriodide*, being formed. The latter crystallises in large, transparent plates, with 1 mol. H_2O , and melts at 54° , the anhydrous substance melting at 155° ; with potash, it yields *dimethylamidomethylthiazole*, which is a crystalline compound and melts at 96° . *Trimethylamidomethylthiazolium iodide*, $\text{C}_4\text{NSH}_4\cdot\text{NMe}_3\text{I}$, is obtained on heating the dimethyl base in sealed tubes with methyl iodide; it is a white solid which melts at 85° , and is not decomposed when boiled with potash.

Acetylmethylamidomethylthiazole, $\text{C}_4\text{NSH}_4\cdot\text{NMeAc}$, is produced by acting on the monomethyl base with acetic anhydride; it crystallises in white needles with 6 mols. H_2O , and melts at 50° , the anhydrous compound, however, melts at 113° . The existence of this derivative, and the fact that a diacetyl-derivative cannot be obtained from this compound is strong evidence in favour of the formula suggested, and that thiocyanopropimine is meso-amidomethylthiazole. The acetyl-derivative of amidomethylthiazole forms salts with alkaline hydroxides, the sodium salt, $\text{C}_6\text{H}_7\text{NaN}_2\text{SO} + 8\text{H}_2\text{O}$, is obtained by warming it with concentrated soda. The formation of this compound and the non-formation of a salt in the case of the monomethylacetyl-derivative, are further proofs in favour of the author's formula, as is also the behaviour of dimethylamidomethylthiazole towards bromine; when this last-named compound is treated with bromine-water, only one hydrogen-atom is displaced. The bromo-derivative, $\text{C}_6\text{H}_5\text{BrN}_2\text{S}$,

crystallises from alcohol and melts at 114° . Amidomethylthiazole and methylamidomethylthiazole are completely destroyed by bromine.

Since thiocyanacetone yields mesoamidomethylthiazole when treated with ammonia, it must be represented by the formula $\langle \begin{smallmatrix} \text{N} : \text{C}(\text{OH}) \\ \text{CMe} : \text{CH} \end{smallmatrix} \rangle \text{S}$, and not by $\text{COMe} \cdot \text{CH}_2 \cdot \text{SCN}$, that given to it by Tscherniac and Norton (*loc. cit.*). It was obtained by their method in crystalline needles melting at 98° ; with phenylhydrazine acetate, hydroxylamine, and sodium hydrogen sulphite, it does not react like a ketone, but with phosphorous pentachloride it acts like a phenol. The hydroxyl-group reacts very readily, and can be displaced by amines; by the action of aniline, *anilidomethylthiazole*, $\text{C}_4\text{NSH}_4\text{NHPh}$, is obtained; it crystallises from alcohol and melts at 117° . *Paratoluidomethylthiazole* melts at 125° ; with metaplylenediamine, the compound, $\text{C}_6\text{H}_4(\text{NHC}_4\text{NSH}_4)_2$, melting at 152° , is obtained.

By the action of metallic thiocyanates on ethyl monochloroacetate, *ethyl hydroxymethylthiazolecarboxylate*, $\langle \begin{smallmatrix} \text{N} : \text{C}(\text{OH}) \\ \text{CMe} : \text{C}(\text{CO} \cdot \text{OEt}) \end{smallmatrix} \rangle \text{S}$, is formed, a molecular change taking place similar to that occurring in the formation of hydroxymethylthiazole; this ethereal salt melts at 128° , and, judging from its behaviour towards phenylhydrazine, does not contain a ketone-group. A compound, $\text{C}_{14}\text{H}_{16}\text{O}_5\text{N}_2\text{S}_2$, which melts at 142° , is also formed in this reaction. F. S. K.

Bromobenzenes. By A. J. LEROY (*Bull. Soc. Chim.*, **48**, 210—216).—Benzene, 450 grams, and aluminium chloride, 25 grams, are mixed in a large flask, and the calculated quantity of bromine is added gradually, care being taken to keep the benzene in large excess. The product is treated with dilute hydrochloric acid, separated, and dried. In this way, monobromobenzene is obtained almost free from the derivative.

Dibromobenzene is obtained in a similar manner, using benzene, 240 grams, bromine, 960 grams, and aluminium chloride, 30 grams. When treated with water, crystals of paradibromobenzene melting at 89° are obtained, together with a small quantity of the tri-derivative, which can be separated by fractionation. The liquid product is mainly dibromobenzene, which boils at 219° and does not solidify at -20° , mixed with some of the monobromo-derivative. The mixture is cooled to remove the para-derivative, and then treated with fuming sulphuric acid and ordinary sulphuric acid, in which the liquid readily dissolves. The product is treated with water to separate the para-derivative, and the liquid is distilled in a current of steam, when metadibromobenzene boiling at 200° is obtained, the yield being equal to about 10 per cent. of the bromine taken. The action of chlorine on benzene, in presence of iodine, yields the ortho- and para-derivatives. With aluminium chloride, no other derivative is obtained. It would seem, therefore, that in the reactions in presence of aluminium chloride there is a tendency to the formation of para- and meta-derivatives.

Paradibromobenzene, when treated with methyl chloride in presence of aluminium chloride, is mainly converted into carbonaceous pro-

ducts; the liquid products, besides monobromobenzene, meta- and para-di-bromobenzene, contain two tribromobenzenes melting at 44° and 119.6° respectively, and yielding nitro-derivatives which melt at 93.5° and 125° respectively.

It would seem that the aluminium chloride first reduces the para-di-bromobenzene to the monobromo-derivative, part of the bromine becoming free and acting on the mono-derivative with formation of the meta-di-derivative. At the same time, another portion of the liberated bromine forms tri-derivatives. These results are analogous to those obtained by Friedel and Crafts by the action of aluminium chloride on dichlorobenzene.

C. H. B.

Action of Sulphuric Acid on Chlorobenzenes. By ISTRATI (*Bull. Soc. Chim.*, **48**, 35—41).—300 grams of pentachlorobenzene was heated with 2000 c.c. of Nordhausen acid for seven to eight hours per day during 15 days. Hydrogen chloride, sulphurous anhydride, and some water, were given off. At the end of 15 days, the acid was decanted off, a fresh quantity added, and the heating continued 15 days longer. No carbonisation took place, but a deep maroon-coloured substance gradually separated. The acid was neutralised by barium carbonate but no sulphonic acid was obtained.

The maroon-coloured substance, after being washed with water, dissolved completely and rapidly in sodium or potassium hydroxide solution, forming a deep red liquid, and when this was filtered and acidified with hydrochloric or sulphuric acid, the substance was reprecipitated. When dried at 60° , it contracts and becomes dark green with a metallic lustre. It is insoluble in boiling water, which removes traces of a colourless, crystalline substance, but it is soluble in concentrated alcohol, very slightly soluble in ether, chloroform, or carbon bisulphide, quite insoluble in benzene. The alcoholic solution, which is cherry-red by transmitted light and yellowish-green by reflected light, and has very great tinctorial power, deposits no solid on cooling, hence it seems probable that a compound is formed. The substance will not crystallise from alcohol, and is not fusible. When heated to redness, it burns and leaves a residue of carbon which is only combustible at a very high temperature. It contains 36.83 per cent. of chlorine, and is free from sulphur. The potassium salt is deep brown with a metallic lustre, and is readily soluble in water, forming a deep red, non-dichroic solution. The barium, iron, tin, mercury, aluminium, magnesium, cadmium, nickel, and other salts, are obtained by double decomposition. They are all pale or deep red, and are insoluble in water, with the exception of the silver salt, which blackens rapidly, and of the mercuric salt, which separates slowly from the solution. The compound seems to have a phenolic function, and the author proposes to call it *Francein*.

Francein is readily attacked and dissolved by cold fuming nitric acid. When heated in sealed tubes at 150° to 180° for six hours, large, colourless crystals, separate. Francein can also be obtained by the action of ordinary concentrated sulphuric acid, and in this case another substance of the same composition as francein, but much more soluble, is also formed at the same time.

Tetrachlorobenzene (200 c.c.), when heated to boiling with concentrated sulphuric acid (1200 c.c.) for 105 hours, is completely dissolved with evolution of water, hydrogen chloride, and large quantities of sulphurous anhydride. No sulphonic acid is formed, but the chief product is a colouring matter which retains a volatile substance; this sublimes at 100° , crystallises in slender needles, and has an odour resembling that of benzoic acid. This substance is removed by treatment with boiling water, when a reddish-brown solid is left easily soluble in alkalis. A considerable portion is soluble in boiling water and especially in alcohol, forming a solution which is pale-brown by transmitted light, and dull-green by reflected light. The more soluble portion contains 33.12 per cent. of chlorine; the portion insoluble in water contains 38.72 per cent.

In the preparation of trichlorobenzenesulphonic acid, when the sulphuric acid is diluted with water, it yields a red product insoluble in water, but easily soluble in alcohol; this is infusible and very dark-coloured with a metallic lustre.

The formation of hydrogen chloride and sulphurous anhydride in these reactions is of special interest. It is probable that under the influence of the sulphuric acid, which plays the part of an oxidising agent, part of the chlorine leaves the benzene nucleus, the sulphuric acid being reduced. This action, which is quite secondary with the lower chlorobenzenes, becomes the dominant reaction with the higher derivatives. In the case of the trichloro-derivative, both reactions are well marked.

When pentachloronitrobenzene is heated with concentrated sulphuric acid, water and hydrochloric acid are given off in large quantities, but very little sulphurous anhydride is liberated. On diluting with water, a crimson precipitate forms. This substance is not soluble in alkalis, but dissolves in warm alcohol from which it separates on cooling. A dilute alcoholic solution is golden-yellow by reflected light and pale-red by transmitted light. C. H. B.

Nitrochloroethylbenzenes. By ISTRATI (*Bull. Soc. Chim.*, **84**, 41—43).—Paradichlorethylbenzene when boiled with concentrated sulphuric acid and fuming nitric acid for 50 hours, fresh nitric acid being added each day, yields a solid, crystalline product completely soluble in the warm acids, from which it is precipitated by adding water. This nitro-derivative is readily soluble in a mixture of alcohol one part and ether two parts. When treated with boiling water, the compound, $C_6H_2Cl_2Et \cdot NO_2$, is dissolved and is deposited on cooling. It is very soluble in alcohol and ether, and crystallises in lamellæ melting at 175° . Its solution is feebly acid, and is not precipitated by lead salts, and is not oxidised by potassium permanganate in the cold. Ferric chloride gives an abundant yellowish-white precipitate.

The portion less soluble in water has the composition $C_6Cl_2Et(NO_2)_3$, and is easily soluble in alcohol, ether, and benzene. It forms small hard crystals which melt at about 195° with partial decomposition. The alcoholic solution mixed with an aqueous solution of ferric chloride yields a slight precipitate after some time.

100 grams of the compound $C_6H_2Cl_2Et \cdot NO_2$ was boiled for 12 hours

with 500 c.c. of fuming nitric acid, and then with a mixture of fuming nitric and sulphuric acids. The product consists of two isomerides which can be separated by treatment with warm alcohol. The less soluble compound forms hard, white crystals which dissolve in ether and melt at 82° . The more soluble compound has a strong aromatic odour and forms crystals melting at 150° . These compounds contain 24 per cent. of chlorine. C. H. B.

Orthocyanotoluene. By S. GABRIEL and B. WEISE (*Ber.*, **20**, 3197—3199).—*Orthocyanobenzal chloride*, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CHCl}_2$, is prepared by boiling the oil obtained in the preparation of orthocyanobenzyl chloride (*Abstr.*, 1887, 1035), whilst chlorine is being passed through. It boils at 260° . When heated with fuming hydrochloric acid at 170° , orthophthalaldehydic acid, melting at 97° , is formed. Strong sulphuric acid converts it into diphtalide ether (m. p. 221°).

Orthocyanobenzotrichloride, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CCl}_3$, is obtained by the further action of chlorine on the oil from cyanobenzene chloride, and crystallises from alcohol in monoclinic crystals of a vitreous lustre; $a : b : c = 1.5464 : 1 : 1.1056$; $\beta = 73^{\circ} 53'$. It melts at 94 — 95° , and boils at about 280° . N. H. M.

Action of Nitric Acid on Pentamethylbenzene. By M. GOTTSCHALK (*Ber.*, **20**, 3286—3288).—When oxidised with dilute nitric acid, pentamethylbenzene yields *tetramethylbenzenecarboxylic acid*, $\text{C}_6\text{HMe}_4\cdot\text{COOH}$ [$\text{COOH} : \text{Me}_4 = 1 : 2 : 3 : 4 : 5$]. This acid crystallises from alcohol in colourless needles, and melts at 165° . Its barium salt crystallises in anhydrous scales or in tufts of needles, $(\text{C}_{11}\text{H}_{13}\text{O}_2)_2\text{Ba} + 2\text{H}_2\text{O}$. When the barium salt is heated with lime, it yields prehnitene. Small quantities of polybasic acids were also formed but were not examined.

When dissolved in cold fuming nitric acid, pentamethylbenzene yields dinitroprehnitene. The author believes that the reaction is analogous to that noticed by Jacobsen (*Abstr.*, 1886, 694), when durene is treated with fuming sulphuric acid, but he has not been able to isolate hexamethylbenzene from the products of the reaction. *Nitropentamethylbenzene*, $\text{C}_6\text{Me}_5\cdot\text{NO}_2$, is obtained by the slow action of bromine vapour on a mixture of pentamethylbenzene and silver nitrate at ordinary temperatures. It crystallises from alcohol in long needles melting at 202° . L. T. T.

Phenylacetylene and Diphenyldiacetylene. By A. F. HOLLEMAN (*Ber.*, **20**, 3080—3082).—Phenylacetylene is prepared by boiling monobromocinnamene with alcoholic potash. The bromocinnamene was obtained from ethylbenzene by the method of Friedel and Bahlson (*Bull. Soc. Chim.*, **35**, 55).

Diphenyldiacetylene is prepared by the method of v. Baeyer and Landsberg (*Ber.*, **15**, 57); it melts at 88° (not 97° , Glaser, *Annalen*, **154**, 151). Bromine (4 mols.) acts on diphenyldiacetylene (1 mol.) with formation of a tetrabromide melting at 173° , and a compound melting at 149 — 153° ; analyses of the latter point to the formula $\text{C}_{16}\text{H}_{10}\text{Br}_2\cdot\text{C}_{16}\text{H}_{10}\text{Br}_4$. N. H. M.

Iodophenols. By E. NÖLTING and T. STRICKER (*Ber.*, **20**, 3018—3023; compare this Journal, 1874, 259; *Zeit. für Chem.* [2], **4**, 322).—Orthiodophenol remains practically colourless after two years' exposure to the air and light. When treated with nitric acid, iodine is set free, but chloriodophenol is formed if chlorine is passed through its solution in carbon bisulphide. When fused with potassium hydroxide, orthiodophenol yields catechol free from resorcinol, even at temperatures above 250°.

Metiodophenol is formed by the usual reactions from metiodonitrobenzene and metamidophenol; it is necessary to diazotise metiodaniline in an excess of acid, otherwise a compound is obtained which crystallises in red needles, melts at 145°, and is possibly diiodoxyazobenzene, $C_6H_4I \cdot N_2 \cdot C_6H_3I \cdot OH$. Metiodophenol crystallises from light petroleum in white needles melting at 39°, or sublimes in small, snow-white needles melting at 40°. It is readily soluble in the usual solvents, does not liberate iodine when treated with chlorine or fuming nitric acid, even when boiled with the latter, and on fusion with potassium hydroxide yields resorcinol free from catechol.

Pariodophenol is readily obtained from paramidophenol. It forms long needles, melts at 93—94°, yields iodine when treated with nitric acid, but not with chlorine, and on fusion with potassium hydroxide at higher temperatures, yields resorcinol instead of quinol.

To explain the formation in fusions with potash or soda of resorcinol from ortho- and para-derivatives, and of catechol from meta-derivatives without assuming the occurrence of intramolecular change, Nöling, recalling the fact that fused alkalis sometimes act as oxidising, and sometimes as reducing agents, suggests that both these actions occur during fusion; 1 : 3 bromophenol, for example, being first oxidised to 1 : 2 : 3 dihydroxybromobenzene, which is then reduced to catechol.

W. P. W.

Solid Orthiodophenol from Iodine and Sodium Phenoxide. By C. SCHALL (*Ber.*, **20**, 3362—3364).—When the orthiodophenol obtained by the action of iodine on sodium phenoxide (*Abstr.*, 1883, 1109) is kept for some months, crystals separate, melting at 42—43°. These dissolve sparingly in hot water, and separate as an oil which crystallises when a crystal is added. It then melts at 39—40°. An iodine determination and the vapour-density show that the substance is pure orthiodophenol. The crystals are at first lustrous and transparent, but become slightly red when exposed to air; they are doubly refractive, and are probably monoclinic (compare Neumann, *Annalen*, **241**, 67).
N. H. M.

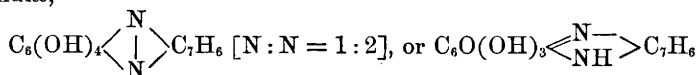
Occurrence of Catechol in Raw Beet-sugar. By E. O. v. LIPPMANN (*Ber.*, **20**, 3298—3301).—The author has examined a sample of raw beet-sugar which showed a strong reducing action on Fehling's solution, but from its mode of manufacture could not contain invert-sugar. An ethereal extract yielded small quantities of catechol and of an acid, $C_9H_{10}O_4$, which showed most of the properties of catechol, and yielded that substance when heated. The author cannot tell whether these substances were derived from the beetroot, or were

formed by the decomposition of part of the carbohydrates during the process of manufacture.

Catechol reduces Fehling's solution, but not Soldaini's solution, and the author therefore advises the use of the latter in preference to Fehling's solution in sugar testing.

L. T. T.

Hydroxyquinones. By R. NIETZKI and F. KEHRMANN (*Ber.*, **20**, 3150—3153).—The authors try to prove experimentally that the formula of tetrahydroxyquinone is, $C_6(OH)_4O_2$ [$O : O = 1 : 4$], and that of rhodizonic acid, $C_6(OH)_2O_4$ [$OH : OH = 3 : 6$]. By mixing an aqueous solution of tetrahydroxyquinone with a salt of orthotoluylenediamine, and adding sodium acetate, a green, crystalline substance is precipitated. This dissolves in alkalis and dilute mineral acids; when dried at increased temperatures, it turns brown, and is ultimately converted into the azine of rhodizonic acid; when oxidised it yields diquinoylazine, $C_6O_4N_2C_7H_6$. From its marked basic properties, it was thought that only one nitrogen-atom had entered into reaction, and that its formula was $C_6(OH)_4O : NC_7H_6NH_2$, analysis showed, however, that its true composition was $C_{13}H_{10}N_2O_4$, and two formulæ,



[$N : NH : O = 1 : 2 : 4$], are suggested. Now if tetrahydroxyquinone is an orthoquinone, it would react with diamines even when the hydrogen of the hydroxyl-group is displaced; but with tetrabenzoyltetrahydroxyquinone no reaction takes place. By heating tetrahydroxyquinone with acetic chloride, a yellow, crystalline *diacetyl*-derivative, $C_6O_2(OAc)_2(OH)_2$, is obtained; it melts at 205° , is soluble in alcohol and ether, but less readily in water; it acts like a bibasic acid, and with orthotoluylenediamine yields a compound very similar to that obtained from tetrahydroxybenzene; it is moreover, in its whole behaviour, very similar to chloranilic acid, and has therefore the constitution [$(OH)_2 : (OAc)_2 = 2 : 5 : 3 : 6$]. From these results, it follows that tetrahydroxyquinone is a paraquinone, and that the second of the above formulæ shows the constitution of the compound formed with orthotoluylenediamine.

F. S. K.

Dinitrosoresorcinol. By S. v. KOSTANECKI (*Ber.*, **20**, 3133—3137).—As paraquinon-oximes are obtained by acting on monhydric phenol-derivatives with nitrous acid, it is usually accepted that when more than one isonitroso-group enters into a polyhydric phenol, each takes up the para-position with respect to a hydroxyl-group. The symmetrical formula $C_6H_2O_2(NOH)_2$ [$O_2 : (NOH)_2 = 1 : 3 : 5 : 6$] has therefore been given to dinitrosoresorcinol, and its correctness is the subject of this research.

Resorcinol and orcinol give dinitroso-compounds when treated with only one molecule of nitrous acid, but from betorecinol $C_6H_2Me_2(OH)_2$ [$Me_2 : (OH)_2 = 1 : 4 : 3 : 5$] a mono-derivative only is obtained even with an excess of nitrous acid, and this abnormal behaviour can only be explained by the supposition that the methyl

radicle occupies the position which would be taken up by the second isonitroso-group. The formula of dinitroso-orcinol is therefore $C_6HMe(NO_2)_2$ [$Me : (NO_2)_2 : O_2 = 1 : 2 : 4 : 3 : 5$], and of dinitrosoresorcinol, $C_6H_2(NO_2)_2$ [$(NO_2)_2 : O_2 = 1 : 3 : 2 : 4$]. These formulæ are supported by the behaviour of cresorcinol, $C_6H_3Me(OH)_2$ [$Me : (OH)_2 = 1 : 2 : 4$], towards nitrous acid, a dinitroso-derivative being produced. Since in cresorcinol there is only one para-position free, it is probable that the symmetrical formula for dinitrosoresorcinol is wrong. *Dinitrosoresorcinol* was obtained in the form of a pale-green substance, which crystallises with 1 mol. H_2O . When heated in a capillary tube above 160° , it explodes; it is sparingly soluble in water and alcohol, insoluble in ether, chloroform, and benzene. Nitric acid oxidises it to *dinitrocresorcinol*, $C_6HMe(NO_2)_2(OH)_2$, which crystallises in long, yellow needles, and melts at 90° , it is sparingly soluble in cold, more readily in hot water, readily soluble in ether or alcohol; it imparts a bright-yellow colour to animal fibres. It is probable that dinitrosoresorcinol has the formula $C_6HO_2(NO_2)_2Me$ [$O_2 : (NO_2)_2 : Me = 1 : 3 : 2 : 4 : 6$], and that dinitrosoresorcinol has an analogous constitution, namely [$O_2 : (NO_2)_2 = 1 : 3 : 2 : 4$].

F. S. K.

Action of Nitrous Acid on Anethoïl. By P. TOENNIES (*Ber.*, 20, 2982—2987).—The compound of anethoïl and nitrous acid, $OMe \cdot C_6H_4 \cdot C_3H_5(N_2O_3)$ (Abstr., 1879, 35, 517), as already described (Abstr., 1881, 167), when heated with alcohol or aqueous potash, yields an isomeric, crystalline product, which dissolves readily in alkalis, but is precipitated by acids from the solution, with the loss of the elements of a molecule of water, in the form of a well-crystallised compound, $OMe \cdot C_6H_4 \cdot C \begin{smallmatrix} \text{CMe} \\ \text{N}_2\text{O}_2 \end{smallmatrix}$. This substance, by the action of alcoholic potash, is converted into an isomeric compound, which readily yields methoxycyanobenzene, $OMe \cdot C_6H_4 \cdot CN$, when heated with hydrochloric acid. The compound of anethoïl and nitrous acid, in addition, forms an acetate,



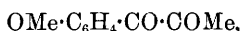
when treated with acetic chloride, and on these grounds is now regarded by the author as an isonitroso-derivative of the formula $OMe \cdot C_6H_4 \cdot C(N \cdot OH) \cdot CMeH(ONO)$. The acetate cannot be distilled in a vacuum without undergoing decomposition into acetic acid and the nitrosoketone, $OMe \cdot C_6H_4 \cdot C(N \cdot OH) \cdot COMe$, which forms an oil readily crystallising in yellow needles. This compound is easily decomposed by boiling hydrochloric acid, yielding hydroxylamine and the diketone $OMe \cdot C_6H_4 \cdot CO \cdot COMe$, which can also be obtained by treating the compound of anethoïl and nitrous acid with hydrochloric acid in the cold; it is a yellow oil, and reacts with phenylhydrazine to form the beautifully crystalline dihydrazide,



The isonitrosoketone is obtained also when the compound of anethoïl

and nitrous acid is treated with alcoholic potash, and the product, after the evolution of nitrous oxide has ceased, is dissolved in water and precipitated by hydrochloric acid. On reduction, it is converted into two compounds, one of which is the base $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHAc}\cdot\text{NH}_2$, and the second is the ketone $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Ac}$, derived from this by loss of ammonia. This ketone is an oil of pleasant odour, boils at 264° , and yields an oily compound with phenylhydrazine. The ketonic base also forms a condensation compound with phenylhydrazine, and is converted into the acetate, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHAc}\cdot\text{NHAc}$, by the action of acetic anhydride, whilst its solution in hydrochloric acid, if treated with aqueous potash, yields a condensation compound, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH} < \begin{smallmatrix} \text{CMe} : \text{N} \\ \text{N} : \text{CMe} \end{smallmatrix} > \text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$. This tertiary base does not react with acetic acid or nitrous acid, but forms with methyl iodide at 100° a beautifully crystalline hydriodide of a mono-methylated base; on heating this it is readily converted into methyl iodide and the original base, but forms with aqueous soda a scarlet-red powder yielding well-crystallised salts with hydrochloric acid and platinic chloride.

The addition product of cinnamene and nitrous acid, $\text{C}_2\text{H}_3\text{Ph}(\text{N}_2\text{O}_3)$, exhibits properties very similar to those of the anethoil compounds. By reduction, it yields a base, $\text{C}_2\text{H}_3\text{Ph}(\text{OH})\cdot\text{NH}_2$, and on treatment with sulphuric acid, is converted into phenylnitroethylene with the evolution of nitrous oxide. When the cinnamene additive compound is treated with aniline, nitrous oxide is also evolved, and a new base probably of the formula $\text{NHPh}\cdot\text{CH}(\text{OH})\cdot\text{CPh}:\text{NOH}$ is obtained; this is decomposed by hydrochloric acid into benzaldehyde, benzonitrile, and aniline. A similar reaction also occurs when ammonia and methylamine are employed instead of aniline, and in this respect the cinnamene compound differs from the anethoil-derivative, since the latter when treated in like manner with ammonia and methylamine yields, with evolution of nitrous oxide, the diketone,



as chief product, only small quantities of the bases



and $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NOH})\cdot\text{CHMe}\cdot\text{NHMe}$ being obtained. The research is being continued. W. P. W.

Action of Phosphorous Pentasulphide on Aniline. By A. KNOP (*Ber.*, 20, 3352–3353). When phosphorous pentasulphide is heated with aniline at a temperature not exceeding 150° , and the product is steam-distilled and crystallised from alcohol, the compound $\text{PS}\cdot\text{C}_{18}\text{H}_{18}\text{N}_3$ is obtained in monoclinic crystals, melting at 153° ; the reaction is accompanied by a violent evolution of hydrogen sulphide.

Chevrier (*Zeit. für Chem.*, 1868, 569), by the action of phosphorus sulphochloride on aniline, obtained an amorphous compound melting at 78° , of the same percentage composition as that described above.

N. H. M.

Sandmeyer's Reaction. Substitution of Cyanogen for the Amido-group. By F. AHRENS (*Ber.*, **20**, 2952—2958).—The three isomeric amidophenols, when diazotised and heated with Sandmeyer's solution of potassium cyanide and copper sulphate (*Abstr.*, 1885, 149), are readily converted into the corresponding cyanophenols (compare next Abstract). To obtain a good yield of orthocyanophenol, it is necessary to separate the diazochloride of orthamidophenol before treatment by Sandmeyer's method, but this step can be omitted in the other two cases. Orthanisidine can in like manner be converted into cyananisoil.

Paramidoacetophenone, on similar treatment, yields *cyanacetophenone*, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$. This crystallises in white needles, melts at $60-61^\circ$, is insoluble in water, but readily soluble in alcohol and ether, and on hydrolysis is converted into Meyer's acetylbenzoic acid (m. p. = 200°). The *oxime*, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}\cdot\text{NOH}$, crystallises in white scales melting at 160° . Paramidobenzophenone, under like conditions, forms a *cyanobenzophenone*, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$, crystallising in yellowish-white granules melting at $107-108^\circ$, and this, on hydrolysis, yields parabenzoylbenzoic acid. The *oxime*, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{NOH}$, crystallises in white scales and melts at 176° .

When paramidodimethylaniline is similarly treated, and the product extracted with ether, an oil is obtained which could not be purified, but probably consists of dimethylamidobenzonitrile, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, since, on hydrolysis with alcoholic potash, it yields an acid identical with Michler's paradimethylamidobenzoic acid.

The author has not succeeded in converting sulphanilic acid into cyanobenzenesulphonic acid by this reaction. W. P. W.

Orthocyanophenol. By V. MEYER (*Ber.*, **20**, 3289).—Repeating Ahrens' experiments on the effect of Sandmeyer's reaction on amidophenol, the author entirely failed to get the cyanophenol described by Ahrens (preceding Abstract), but obtained salicoutrile (Tiemann, this vol., p. 276). L. T. T.

Derivatives of Paramidoisobutylbenzene. By C. GELZER (*Ber.*, **20**, 3253—3259).—*Nitracetylamidoisobutylbenzene*,



is obtained on nitrating acetylamidoisobutylbenzene at 0° ; it crystallises in slender, yellow needles, and melts at $250-252^\circ$, with some decomposition. When reduced, an anhydro-base seems to be formed.

Nitramidoisobutylbenzene, $\text{C}_4\text{H}_9\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{NH}_2$, prepared by the action of cold alcoholic potash on the acetyl-compound, crystallises in yellowish-red, short needles or plates, melts at 106.5° , is only sparingly soluble in hot water, readily in alcohol, benzene, and ether. The salts are very soluble, and are not characteristic.

Diamidoisobutylbenzene, $\text{C}_4\text{H}_9\cdot\text{C}_6\text{H}_3(\text{NH}_2)_2$, obtained by the reduction of the preceding compound, crystallises in micaceous, colourless scales or tables, melts at 97.5° , distils at $280-282^\circ$, and is sparingly soluble in cold, readily soluble in hot water and in alcohol, ether, and benzene. The *hydrochloride*, $\text{C}_{10}\text{H}_{16}\text{N}_2\cdot 2\text{HCl}$, forms lustrous, white

plates; the *picrate* crystallises in slender, yellow needles; the oxalate forms thin, white plates. Like other orthodiamines, it forms compounds with phenanthraquinone and benzil.

Phenanthraisobutylphenazine, $\begin{array}{c} \text{C}_6\text{H}_4\cdot\text{C}\cdot\text{N} \\ | \quad \parallel \\ \text{C}_6\text{H}_4\cdot\text{C}\cdot\text{N} \end{array} \rangle \text{C}_6\text{H}_3\cdot\text{C}_4\text{H}_9$, prepared by

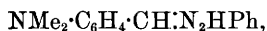
adding the diamido-base to a solution of phenanthraquinone in glacial acetic acid, crystallises in pale-yellow, interlaced needles, melts at 146.5° , and is very sparingly soluble in hot water or cold alcohol, readily in ether or benzene. It is not decomposed when boiled with hydrochloric acid. With concentrated sulphuric acid, it gives a characteristic cherry-red coloration.

Benziloisobutylphenazine, $\begin{array}{c} \text{CPh}\cdot\text{C}\cdot\text{N} \\ | \quad \parallel \\ \text{CPh}\cdot\text{C}\cdot\text{N} \end{array} \rangle \text{C}_6\text{H}_3\cdot\text{C}_4\text{H}_9$, forms nearly white,

slender needles, melts at 144° , is insoluble in water, moderately soluble in alcohol, and readily in benzene, ether, and carbon bisulphide. It has very feeble basic powers, but a hydrochloride, $(\text{C}_{24}\text{H}_{22}\text{N}_2)_2\cdot\text{HCl}$, is described; it forms a greenish, crystalline powder, and is decomposed when dissolved. A. J. G.

Condensation of Chloral Hydrate with Tertiary Aromatic Amines. By O. KNÖFLER and P. BOESSNECK (*Ber.*, 20, 3193—3195).—The compound, $\text{CCl}_3\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ (*Abstr.*, 1886, 458), is best prepared by treating a solution of 200 grams of chloral hydrate in 300 grams of dimethylaniline with 110 grams of powdered zinc chloride. After some weeks, the viscous mass becomes crystalline. The base is then converted into the hydrochloride. The yield is 82 per cent. of the theoretical. The *sulphate* crystallises in cubes more soluble than the hydrochloride.

Paradimethylamidobenzylidene-phenylhydrazine,



crystallises in needles melting at 148° .

Paradimethylamidobenzaldoxime, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$, crystallises in yellowish-brown plates melting at 144° . N. H. M.

Action of Aromatic Diamines on Sugar. By P. GRIESS and G. HARROW (*Ber.*, 20, 3111—3118).—*Arabino-orthodiamidobenzene*, $\text{C}_6\text{H}_4\langle\begin{array}{c} \text{NH} \\ \text{NH} \end{array}\rangle\text{C}_5\text{H}_8\text{O}_4$, is obtained by mixing aqueous solutions of orthodiamidobenzene (1 mol.) and arabinose (2 mols.). The whole is evaporated nearly to dryness, water being added as it evaporates until the amount of crystals no longer increases. It crystallises from boiling water in small, white needles, which melt with decomposition at 235° ; it is sparingly soluble in boiling water, less soluble in alcohol, and almost insoluble in ether. It has a slightly bitter taste, does not reduce Fehling's solution, and is dextrorotatory. Aqueous potash dissolves it readily. Boiling concentrated hydrochloric acid and boiling aqueous potash have no action on it. The *hydrochloride* crystallises from water, in which it is readily soluble, in globular groups

of very small plates. It is sparingly soluble in dilute hydrochloric acid. The *hydrobromide* resembles the hydrochloride. The formation of arabinodiamidobenzene is similar to that of gluco-orthodiamidobenzene (Abstr., 1887, 930), assuming arabinose to have the formula $C_5H_{10}O_5$ (Kiliani, Abstr., 1887, 465).

Arabinometaparadiamidotoluene, $C_6H_3Me<\begin{smallmatrix} NH \\ NH \end{smallmatrix}>C_5H_8O_4$, prepared similarly to the compound above described, crystallises in small, white needles having a slightly bitter taste. It melts at 238° , and is more sparingly soluble than the orthodiamidobenzene-derivative, to which it is in other respects very similar.

Arabino- γ -diamidobenzoic acid, $COOH \cdot C_6H_3<\begin{smallmatrix} NH \\ NH \end{smallmatrix}>C_5H_8O_4 + 2H_2O$, crystallises in needles melting with decomposition at 235° . It is sparingly soluble in boiling water, less soluble in alcohol. It is dextrorotatory, reddens litmus, and does not reduce Fehling's solution. The barium salt is a white, amorphous substance; the silver salt forms a white, sandy powder. The *hydrochloride* crystallises from dilute hydrochloric acid in small, white needles; it is decomposed by water.

Galacto-orthodiamidobenzene, $C_6H_4<\begin{smallmatrix} NH \\ NH \end{smallmatrix}>C_6H_{10}O_5$, resembles the arabino-derivative in physical and chemical properties. It melts at 246° with decomposition. The *hydrochloride* with $1\frac{1}{2}$ mol. H_2O , and the *hydrobromide* crystallise in needles and are very readily soluble in water, sparingly soluble in hydrochloric acid.

Galacto- γ -diamidobenzoic acid, $COOH \cdot C_6H_3<\begin{smallmatrix} NH \\ NH \end{smallmatrix}>C_6H_{10}O_5 + H_2O$, crystallises in needles. It completely resembles the corresponding arabino-acid.

N. H. M.

Decomposition of Diazo-compounds. By I. REMSEN and W. R. ORNDORFF (*Amer. Chem. J.*, **9**, 387—399).—Pure and dry diazobenzene nitrate was decomposed by warming it with ten times its weight of absolute alcohol. The several products obtained, calculated on the weight of nitrate taken, were phenetol 16 per cent., orthonitrophenol 7 per cent., dinitrophenol 3.5 per cent., benzene 1.8 per cent., and considerable quantities of tarry matter from which nothing definite could be separated; no aldehyde was observed. Griess had previously noticed the production of nitrophenols, and attributed them to his not having used absolute alcohol, but that this explanation is not correct is shown by the above, and by the fact that dry diazobenzene nitrate when heated with dry toluene yields 20 to 24 per cent. of orthonitrophenol, but no dinitrophenol. Using 50 per cent. alcohol for the decomposition, the quantities of nitrophenols formed are increased, whilst the yield of phenetol and especially of benzene is decreased. Using dry diazobenzene sulphate and absolute alcohol, 30 per cent. of phenetol and 1.5 per cent. of benzene were obtained, and using toluene in place of the alcohol, paraphenol-sulphonic acid is formed. The last decomposition, namely, elimination of nitrogen and rearrangement of the constituents of the mole-

cule, corresponds with that undergone by the nitrate:— $C_6H_5 \cdot N_2 \cdot O \cdot NO_2 = C_6H_4(OH) \cdot NO_2 + N_2$. Phenetol boils at 170° , and when treated with fuming nitric acid yields dinitrophenol (m. p. $86-87^\circ$). This is very nearly the melting point of dinitrobenzene (89.9°), and hence the misstatement that benzene is the principal product of the decomposition of diazobenzene with alcohol.

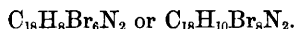
When orthodiazotoluene sulphate is heated with absolute alcohol, the principal product is orthocresyl ethyl ether (30 per cent.); neither toluene nor aldehyde could be detected. With the para-compound, the decomposition is quite different, 18 per cent. of toluene and 11 per cent. of paracresyl ethyl ether being obtained, as well as aldehyde. Metadiazotoluene sulphate and absolute alcohol yield neither aldehyde nor toluene, but metacresyl ethyl ether is formed (55 per cent. reckoned on the metatoluidine employed). The metatoluidine was prepared from paratoluidine by nitrating the acetyl-derivative, eliminating the amido-group, and reducing the metanitrotoluene. In this case, it is to be noticed that the diazo-group is readily displaced by hydrogen, a yield of 68.7 per cent. being obtained.

The authors conclude that the presence of a paraffin residue in the para-position relatively to the diazo-group is favourable to the displacement of the diazo-group by hydrogen. Wroblewski, from a study of the three chlorotoluidines, concludes that in the decomposition of the diazo-compounds by alcohol the normal reaction (production of the hydrocarbon) suffers a change due to the influence of the halogen when it occupies the para-position relatively to some other substituting group. This conclusion is contradicted by the author's experiments. Of the nine recorded cases of mono-substituted amido-benzene compounds that undergo Griess' reaction, eight contain the two groups in the para-position. An examination of the 80 or 90 cases in which two or more groups are present besides the amido-group, and in which the diazo-group is displaceable by hydrogen, also shows that in nearly all cases the amido-group is in the para-position with respect to some other group.

H. B.

Diphenylpara-azophenylene. By E. v. BANDROWSKI (*Monatsh.*, **8**, 475—483).—In a former paper (*Abstr.*, 1886, 1023), the author showed that the product of the oxidation of diphenylamine in alkaline solution is a diphenylpara-azophenylene, $C_6H_4 \langle \begin{smallmatrix} NPh \\ NPh \end{smallmatrix} \rangle$, a view confirmed by its ready hydrogenation into a leuco-product; the latter seems to be identical with Calm's diphenylparaphenylenediamine. To confirm this view, this substance was prepared according to Calm's directions from quinol and aniline heated with a mixture of zinc and calcium chlorides in a sealed tube at $200-210^\circ$. Thus prepared, the melting point of the compound was found to be $132-135^\circ$, instead of 152° as assigned to it by Calm. The same melting point was found for the substance $C_{18}H_{16}N_2$, prepared by the author's method; hence there can be no doubt as to the identity of the two compounds in question. This identity was further confirmed by the conversion of the diphenylparaphenylenediamine, prepared by either method, into the oxidation product of diphenylamine, $C_{18}H_{14}N_2$, which was effected

either directly by moderate oxidation with hydrogen peroxide, or indirectly by decomposition of the dinitroso-derivative in hot alcoholic solution. This dinitroso-derivative, formed by passing nitrous fumes into a cold alcoholic solution of diphenylparaphenylenediamine, forms yellow, glistening crystals, melting at 120° with decomposition. It gives an intense red coloration with sulphur and nitric acid, and is converted by hydrogenation with zinc-dust and acetic acid, into diphenylpara-azophenylene, and on boiling with alcohol, into diphenylpara-azophenylene and nitric oxide. On bromination in chloroform solution, diphenylpara-azophenylene gives a bromo-derivative,



This forms acicular crystals melting at 243° . It dissolves in nitric acid with production of a dirty-green colour. On dilution a reddish precipitate of a dinitro-derivative is obtained, but this probably consists of two isomeric substances.

V. H. V.

Substitution in Azo-compounds. By E. NÖLTING (*Ber.*, **20**, 2992—2998).—Amidoazobenzene yields several crystalline compounds when nitrated, none of which, however, are identical with 1 : 4 or 1 : 3 $\text{C}_6\text{H}_4(\text{NO}_2) \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4\text{NH}_2$. The nitro-group seems to enter the amidated group, since aniline was obtained by the reduction of the compound.

When phenylazodimethylaniline (dimethylamidoazobenzene) is dissolved in concentrated sulphuric acid (66° B.), nitrated in a freezing mixture with a mixture of 50 per cent. nitric acid (1 part) and sulphuric acid (2 parts), and the product poured into water, a *nitro*-derivative, $\text{PhN} : \text{N} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{NMe}_2$, is obtained, which crystallises in black needles with a greenish iridescence, and melts at 198° ; it is insoluble in water, sparingly soluble in alcohol and ether, readily soluble in benzene. It is a feeble base, and on reduction yields aniline and another base, probably dimethyltriamidobenzene. An isomeric *nitro*-derivative, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, is also formed, identical with that prepared by Meldola (*Trans.*, 1884, 107). This crystallises in needles, melts at 225 — 226° , and is sparingly soluble in alcohol, ether, and benzene. On reduction with ammonium sulphide, it yields amido-dimethylamidoazobenzene melting at 186 — 187° , and with tin and hydrochloric acid it is converted into paraphenylenediamine and dimethylparaphenylenediamine.

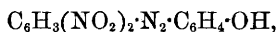
When paratolylazodimethylaniline is nitrated in like manner, it yields a *nitro*-derivative, $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{NMe}_2$, which crystallises in long, bright red needles, melts at 181° , and is sparingly soluble in alcohol and ether, readily soluble in benzene. It is a feeble base, and on reduction is converted into paratoluidine and a readily decomposable base. The isomeric bases, $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2) \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$



crystallising in brownish-red scales melting at 159 — 160° , and $[\text{Me} : \text{NO}_2 : \text{N}_2 = 4 : 3 : 1]$, crystallising in red prisms melting at 146 — 147° , were prepared for purposes of comparison.

If phenylazodimethylaniline is sulphonated with 100 per cent. sulphuric acid at 100°, a sulphonic acid, $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, is formed, identical with that obtained by Möhlau (Abstr., 1884, 1149). Paratolylazodimethylaniline can be sulphonated by dissolving it in 100 per cent. sulphuric acid and heating at 100° with sulphuric acid containing 66 per cent. of sulphuric anhydride; the resulting sulphonic acid, $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, crystallises in violet prisms, and is soluble in hot water and alcohol, yielding, like its salts, red-coloured solutions. On reduction, it is converted into dimethylparaphenylenediamine and metamidoparatoluenesulphonic acid. These experiments were made in conjunction with T. Baumann.

When phenylazophenol (oxyazobenzene) is nitrated under the above conditions, the *nitro*-derivative, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, forms the chief product. This crystallises in reddish-brown needles, melts at 211°, and is identical with that obtained from phenol and diazotised paranitraniline. The isomeric *nitro*-derivatives, $[\text{NO}_2 : \text{N}_2 = 1 : 2]$, crystallising in orange-yellow needles melting at 126°, and $[\text{NO}_2 : \text{N}_2 = 1 : 3]$, crystallising in red needles melting at 155–157°, were also prepared for purposes of comparison. A *dinitro*-derivative,



is also formed during the nitration, and constitutes the chief product if twice the quantity of nitric acid is employed. It crystallises in orange-red needles, melts at 200°, and is identical with the compound obtained from diazotised 1 : 2 : 4 dinitraniline and phenol. These experiments were made in conjunction with T. Stricker.

W. P. W.

Diazoamido-compounds. By E. NÖLTING and F. BINDER (*Ber.*, 20, 3004–3018).—The authors have prepared the diazoamido-compounds from paratoluidine and diazobenzene chloride and from aniline and diazoparatolyl chloride, and have submitted each to the following reactions, comparing the products throughout:—(1.) Reduction at 0° in alcoholic solution with tin and hydrochloric acid: products, aniline, paratoluidine, phenylhydrazine, and paratolylhydrazine. (2.) Bromination in benzene solution in the cold: products, diazoparatoluene bromide and tribromaniline. (3.) Digestion with a mixture of aniline (2 parts) and aniline hydrochloride ($\frac{1}{2}$ part) at 60° until nitrogen was no longer evolved when a sample was treated with dilute sulphuric acid: products, amidoazobenzene and paratoluidine. (4.) Digestion in like manner with dimethylaniline: products, paratolylazodimethylaniline and aniline. (5.) Digestion with excess of phenol and some sodium hydroxide at 60° until nitrogen was no longer evolved when a sample was treated with dilute sulphuric acid: products, phenylazophenol (hydroxyazobenzene) and paratoluidine. The quantity of phenol employed seems to influence the nature of the product (compare Abstr., 1887, 664). (6.) Digestion with excess of dilute sulphuric acid (1 to 10): products, aniline, paratoluidine, phenol, and paracresol. (7.) Ethylation of the compounds, and decomposition of the products by treatment with dilute sulphuric

acid: products, ethylaniline, ethylparatoluidine, phenol, and paracresol. In experiments (3) and (5) the compounds act as if each had the constitution $\text{PhN:N}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, in experiments (2) and (4) as if each had the constitution $\text{C}_7\text{H}_7\text{N:N}\cdot\text{NHPh}$, whilst from experiments (1) and (6) both formulæ must be ascribed to each of the compounds, and in experiment (7) each compound must have contained both isomerides, unless in this experiment a third isomeride has been formed, as Meldola has been led to conclude is the case when diazoamidometanitropropanitrobenzene is ethylated (Trans., 1887, 110, 443). In all these experiments, no difference could be detected between the two compounds in the course of the reactions or in the nature or relative quantities of the decomposition products, and hence Griess' conclusion that they are identical is confirmed.

The compounds formed by the action of diazoparatolyl chloride on ethylaniline, and of diazobenzene chloride on ethylparatoluidine are isomeric. *Paradiazotolyethylanilide*, $\text{C}_7\text{H}_7\text{N:N}\cdot\text{NPhEt}$, is an oil, which cannot be crystallised, and yields paratolyldiazine and ethylaniline on treatment with nascent hydrogen, paracresol and ethylaniline on digestion with dilute sulphuric acid, and paratolylazophenol and ethylaniline on digestion with phenol. *Diazobenzene-ethylparatoluide*,



on the contrary, forms red crystals, melts at $38-39^\circ$, and yields phenylhydrazine and ethylparatoluidine on reduction with nascent hydrogen, phenol and ethylparatoluidine on digestion with dilute sulphuric acid, and phenylazophenol and ethylparatoluidine on digestion with phenol.

The compounds formed by the action of diazobenzene chloride on parabromaniline and of parabromodiazobenzene chloride on aniline are identical, and yield parabromaniline and phenol on digestion with dilute sulphuric acid, a result pointing to the formula



Diazobenzene chloride reacts with β -naphthylamine to form an amido-azo-compound; a diazo-amido-compound, however, is formed by the action of diazo- β -naphthyl chloride on aniline. This crystallises in bright yellow needles, melts at 150° with decomposition, and yields aniline, β -naphthylamine, phenol, and β -naphthol on digestion with dilute sulphuric acid, amido-azobenzene and β -naphthylamine on digestion with aniline, and phenylazophenol and β -naphthylamine on digestion with excess of phenol, the two last results pointing to the formula $\text{PhN:N}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, which does not accord with its method of formation.

The diazo-amido-compound obtained by the action of diazo- α -naphthyl chloride on aniline yields on digestion with dilute sulphuric acid a mixture of aniline, α -naphthylamine, phenol, and α -naphthol.

Diazobenzene chloride does not react with paranitraniline. The diazo-amido-compound formed by the action of diazoparanitrobenzene chloride on aniline crystallises in yellow, silky needles, melts at 148° , and yields phenol and paranitraniline on digestion with dilute sul-

phuric acid, diazobenzene bromide and bromoparanitraniline on bromination, phenylazophenol and paranitraniline on digestion with excess of phenol, and paranitraniline, aniline, amido-azobenzene, and paranitramido-azobenzene, the last in very small quantity, on digestion with aniline.

Diazobenzenepiperide, $\text{PhN:N:N:C}_5\text{H}_{10}$, obtained by the action of diazobenzene chloride on piperidine and sodium acetate in molecular proportion, yields phenol and piperidine on digestion with dilute sulphuric acid, and phenylhydrazine and piperidine on reduction with nascent hydrogen.

Diazobenzenetetrahydroquinolide, $\text{PhN:N:N:C}_9\text{H}_{10}$, obtained in like manner, is a yellow oil, and yields phenol and tetrahydroquinoline when boiled with dilute sulphuric acid. *Diazobenzenemethylanilide*, PhN:N:NMePh , also obtained in like manner, is a yellow oil, which gradually changes, especially if traces of acid are present, into the amido-azo-compound, and yields phenol and methylaniline when boiled with dilute sulphuric acid, and phenylhydrazine and methylaniline on reduction with nascent hydrogen. The compound formed by the reduction of paranitrodiazobenzene chloride on methylaniline is *paranitrophenylazomethylaniline*, $\text{C}_6\text{H}_4(\text{NO}_2)\text{N:N:C}_6\text{H}_4\text{NHMe}$, which crystallises in red needles melting at 134° .

Gasteger has prepared the following:—*Diazoparatolylethylparatoluide*, $\text{C}_7\text{H}_7\text{N:NNEtC}_7\text{H}_7$, a yellow oil yielding paracresol and ethylparatoluidine with dilute sulphuric acid; *diazometanitrobenzene-ethylparatoluide*, $\text{C}_6\text{H}_4(\text{NO}_2)\text{N:NNEtC}_7\text{H}_7$, which crystallises in yellow needles, melts at 55° , and yields metanitrophenol and ethylparatoluidine when boiled with dilute sulphuric acid; *diazoparanitrobenzene-ethylparatoluide*, $\text{C}_6\text{H}_4(\text{NO}_2)\text{N:NNEtC}_7\text{H}_7$, which crystallises in yellow needles, melts at $114\text{--}115^\circ$, and yields paranitrophenol and ethylparatoluidine when boiled with dilute sulphuric acid.

W. P. W.

Constitution of Azimido-compounds. By E. NÖLTING and A.

ABT (*Ber.*, **20**, 2999—3003).—Hitherto Griess' formula, $\text{R} \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ | \\ \text{N} \end{array} \text{NH}$ (Abstr., 1883, 56), for the azimido-compounds has been more generally adopted than the alternative formula, $\text{R} \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{array}$, proposed by Kekulé and by Ladenburg (*Ber.*, **9**, 219); the authors, however, bring forward the following evidence in support of the latter, and in addition point out that the formation of acetylazimidotoluene from acetylorthotoluylenediamine (Abstr., 1886, 874) admits of easy explanation on this theory without assuming an intramolecular change, which is necessary if Griess' formula is employed.

When pure ethyltoluylenediamine hydrochloride $[\text{NEtH:NH}_2:\text{Me} = 1:2:4]$ in concentrated aqueous solution is treated at 0° with sodium nitrite in molecular proportion, *ethylazimidotoluene*, $\text{C}_6\text{H}_3\text{Me:N}_3\text{Et}$, is obtained; this crystallises from alcohol in colourless needles, melts at 147° , and is insoluble in water and alkalis, but soluble in the ordinary organic solvents. The hydrochloride is

decomposed by water; the *platinochloride*, $(C_9H_{12}N_3)_2, H_2PtCl_6$, crystallises in yellow needles.

Azimidotoluene (Ladenburg, *ibid.*), prepared in like manner from pure orthotoluylenediamine hydrochloride, has not only basic but feebly acid properties, since it dissolves in alkalis and can be reprecipitated from the solution by carbonic anhydride. The *sodium*-compound, $C_7H_8NaN_3$, crystallises from benzene in white flocks consisting of small needles, and in solution is only stable in the presence of excess of alkali. When ethylated, azimidotoluene yields a compound identical with the ethylazimidotoluene just described, and inasmuch as two isomeric ethyl-derivatives are theoretically possible (assuming Ladenburg's formula), the authors hold that in this case it is the amido-group in the meta-position relatively to the methyl which is converted into the azo-group when orthotoluylenediamine is diazotised. On fusion with potassium hydroxide, azimidotoluene is converted into amidocresol with the evolution of ammonia.

In a footnote, the authors state ethylnitrotoluidine (Gattermann, Abstr., 1885, 975) can be obtained by nitrating ethylacetotoluide in 4 parts of sulphuric acid and subsequently saponifying; if larger quantities (20 parts) of sulphuric acid are employed, appreciable quantities of the meta-derivative are also formed. W. P. W.

Action of Phenylhydrazine on Members of the Carbamide Series. By S. SKINNER and S. RUHEMANN (*Ber.*, 20, 3372—3374).—When biuret is heated over a small flame with a slight excess of phenylhydrazine, ammonia is evolved, and Pinner's phenylurazole (Abstr. 1887, 1042) is formed, to which the authors ascribe the constitution $NH < \begin{smallmatrix} CO \cdot NH \\ CO \cdot NPh \end{smallmatrix} >$.

Diphenylcarbazine, $CO(NH \cdot NHPh)_2$, is prepared by heating urethane (1 mol.) with phenylhydrazine (2 mols.) for some hours, until the evolution of ammonia ceases. It melts at 151° , is readily soluble in alcohol, sparingly soluble in hot water, insoluble in ether.

Phenylsemithiocarbazine, $NH_2 \cdot CS \cdot NH \cdot NHPh$, formed by the action of phenylhydrazine on monophenylthiocarbamide, crystallises in white needles melting at 190° , readily soluble in hot alcohol, insoluble in water. Ammonia, nitrogen, benzene, and aniline are formed in the reaction. N. H. M.

Dyes which can be Fixed by Mordants. By S. v. KOSTANECKI (*Ber.*, 20, 3146—3149).—Very little is known of the connection existing between the constitution of organic colouring matters and their tinctorial properties, or what determines whether certain acid colouring matters can be fixed by a mordant or not. Experiments were made which seem to show that nitrosophenols can be fixed by a mordant only when they are *ortho*-quinoneoximes, and that other phenol colours can do so only when they contain two hydroxyl radicles in the *ortho*-position. All the dyes which are derived from gallic acid, for instance, anthragallol, gallein, coerulein, galloflavin,

and gallocyanin, owe their tinctorial value to the presence of the ortho-hydroxyl-groups (see also this vol., p. 292). F. S. K.

Products of the Action of Nitric Acid on Acetophenone. By A. F. HOLLEMANN (*Ber.*, **20**, 3359—3362).—Eighty grams of fuming nitric acid (sp. gr. 1.4) is added to 10 grams of acetophenone, and the whole heated at 30—40°; the liquid separates into two layers, of which the upper one becomes crystalline after one to two days. The crystals are washed with water, and extracted with boiling ether. A sparingly soluble nitrogenous substance melting at 177—179° remains undissolved. The ethereal solution yields crystals of a compound, $C_2N_2O_2(COPh)_2$, melting at 87°; it is readily soluble in alcohol and ether, insoluble in water. When treated with potash or sulphuric acid, it yields benzoic acid. It is reduced by zinc-dust and acetic acid to diphenylethylene diketone melting at 143° (not 140°). The compound contains no hydroxyl-group, and can be boiled with acetic chloride for a day without change (compare *Rec. Trav. Chim.*, **6**, 60).

N. H. M.

Methyl Duryl Ketone from Asymmetrical and Symmetrical Durene. By A. CLAUS and C. FOECKING (*Ber.*, **20**, 3097—3104).—The durenens are best prepared as follows:—A mixture of 100 grams of mesitylene (or pseudocumene) and 140 grams of methyl iodide is added to 100 grams of aluminium chloride covered with carbon bisulphide, and the whole heated on a water-bath for five days. The product is treated with water, steam distilled, and the distillate fractionally distilled. The three durenens are separated from one another by freezing.

Unsymmetrical duryl methyl ketone, $C_6HMe_4 \cdot COMe$ [$Me_4 : COMe = 2 : 3 : 4 : 6 : 1$], is prepared in the usual manner by means of aluminium chloride, and forms a colourless strongly refractive liquid of a peculiar odour boiling at 253—255° (uncorr.); it is readily soluble in the usual solvents except water. It distils without decomposition with superheated steam. The *phenylhydrazine compound* forms lustrous, yellowish, matted needles which decompose at 215° without previous fusion. The *hydroxylamine-derivative* crystallises in small plates melting at 148°. When the ketone is reduced with zinc-dust and alcoholic potash, the *carbinol*, $C_6HMe_4 \cdot CHMe \cdot OH$, is obtained; it is a pale-yellow liquid and boils at above 300°.

2 : 3 : 4 : 6 Tetramethylphenylglyoxylic acid, $C_6HMe_4 \cdot CO \cdot COOH$, is formed when the ketone is oxidised with potassium permanganate in dilute aqueous solution in the cold. It is a bright yellow oil, readily soluble in alcohol and ether, sparingly soluble in water. When kept in a freezing mixture for months, it solidifies. Boiling water decomposes it. The *sodium salt* (with 5 mols. H_2O), the *potassium* and *barium* (with 5 mols. H_2O), *calcium* (with 3 mols. H_2O), and other salts were prepared.

2 : 3 : 4 : 6 Tetramethylmandelic acid, $C_6HMe_4 \cdot CH(OH) \cdot COOH$, is prepared by reducing the glyoxylic acid with sodium-amalgam. It crystallises in short, colourless, transparent, lustrous prisms, melting at 156°; it dissolves readily in alcohol and ether, sparingly in water. The *sodium* (with $1\frac{1}{2}$ mol. H_2O) and *potassium salts* are very readily

soluble in water; the *calcium salt* (with 8 mols. H_2O) crystallises in tufts of needles; the *barium salt* (with 3 mols. H_2O) forms small crystals, readily soluble in water.

Symmetrical duryl methyl ketone, $\text{C}_6\text{HMe}_4\cdot\text{COMe}$ [$\text{Me}_4:\text{COMe} = 2:3:5:6:1$], crystallises in white, lustrous plates, melts at 63° (uncorr.), boils at 251° (uncorr.), and distils with steam. The *hydrazine-derivative* forms small, lustrous crystals which at 225° decompose without melting. The *carbinol* crystallises in white plates which melt at 72° .

Symmetrical durylglyoxylic acid crystallises in small, white, lustrous scales which melt at 124° (uncorr.); it is readily soluble, except in water, and cannot be distilled. The alkali salts are very readily soluble; the *potassium* with 5 mols. H_2O , the *calcium* with 9 mols. H_2O , the *barium* with 3 mols. H_2O , and the *silver salts*, are described.

2:3:5:6 Tetramethylmandelic acid, $\text{C}_6\text{HMe}_4\cdot\text{CH}(\text{OH})\cdot\text{COOH}$, melts at 146° (uncorr.), dissolves readily in alcohol, ether, benzene, &c. The *alkali salts* are very readily soluble, and can scarcely be obtained crystalline; the *barium salt* with 2 mols. H_2O , and the *calcium salt* with 8 mols. H_2O , were prepared; the latter crystallises in small, slender needles.

2:3:4:6 Tetramethylbenzoic acid, $\text{C}_6\text{HMe}_4\cdot\text{COOH}$, and the *2:3:5:6 acid* are obtained by oxidising the corresponding duryl methyl ketones with warm permanganate solution. The former is a thick oil, whilst the latter crystallises in plates of a silvery lustre, melting at 109° (uncorr.). N. H. M.

Nitrile of Salicylic Acid. By F. TIEMANN (*Ber.*, **20**, 3082—3084).—*Salicylic acid nitrile* is prepared from the aldoxime of salicaldehyde, or by distilling the thiamide of salicylic acid. It melts at 98° , dissolves readily in alcohol and ether, rather sparingly in water, behaves towards alkalis like a phenol, and gives a reddish-violet coloration with ferric chloride; under diminished pressure, it distils almost without decomposition, and can be readily converted into salicylic acid. The compound prepared by Grimaux (*Bull. Soc. Chim.*, **13**, 25) by fusing salicylamide with phosphoric anhydride, which melts at 195° , is therefore not the normal nitrile of salicylic acid (compare also Ahrens, this vol., p. 266). N. H. M.

Condensation-products from β -Anilido-acids. By A. REISSERT (*Ber.*, **20**, 3105—3110).— *β -Anilido-acrylic acid*, $\text{NHPh}\cdot\text{C}_2\text{H}_2\cdot\text{COOH}$, is obtained by boiling the mixture of anilidomaleic-anilide and anilidomaleic acid (formed from aniline and dibromosuccinic acid, Tiemann and Reissert, *Abstr.*, 1886, 551; Michael, *Abstr.*, 1886, 698; and Reissert, *Abstr.*, 1886, 791), with aqueous potash. The product is precipitated with acetic acid, dissolved in absolute alcohol, and converted into the sodium salt. It melts with partial decomposition at 194° , dissolves readily with alcohol and acetone, and is almost insoluble in water, benzene, and chloroform. The *sodium salt* with $2\frac{1}{2}$ mols. H_2O crystallises in white plates of a silky lustre; the *ethyl salt* melts at 143 — 144° .

γ -Ketodihydroquinoline, $C_6H_4 \langle \begin{smallmatrix} CO \cdot CH \\ NH \cdot CH \end{smallmatrix} \rangle$, is formed when β -anilido-acrylic acid is dissolved in concentrated sulphuric acid, or when the acid is heated for a short time at 200° . The product is several times dissolved in acetone and precipitated with water, and is then crystallised from alcohol, from which it separates in gold-coloured plates melting at 235° . When distilled, a small amount is obtained colourless. It is very sparingly soluble in the usual solvents, and is almost insoluble in acids and alkalis. When distilled over heated zinc-dust, quinoline is formed. N. H. M.

Formation of Anilic Acids from Anhydrides of Bibasic Acids. By R. ANSCHÜTZ (*Ber.*, **20**, 3214—3216).—Fumaranilic acid, $COOH \cdot CH : CH \cdot CO \cdot NHPh$, identical with that prepared from malein-anil, is formed when maleic anhydride, dissolved in ether, is mixed with aniline.

Mesaconanilic acid, prepared from citraconic anhydride, melts at 152 — 153° , and is identical with the product which separates when an aqueous solution of monaniline citraconate is kept.

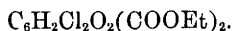
The anilic acid from itaconic anhydride melts at 151 — 151.5° ; it is not identical with the acids obtained by Gottlieb and by Michael by heating itaconic acid with aniline, and by boiling an aqueous solution of monaniline itaconate. N. H. M.

Hydrazocumic Acid. By N. MOLCANOFFSKI (*Chem. Centr.*, 1887, 1162, from *J. Russ. Chem. Soc.*, 1887, 295—297).—Nitrocumic acid was reduced in alkaline solution by an excess of sodium amalgam and the reduction products (mostly the azo- and hydrazo-acids) precipitated by adding hydrochloric acid. They were separated by crystallisation from alcohol, the hydrazo-acid being much less soluble in this medium. *Hydrazocumic acid* forms colourless needles, very stable when dry, but in solution slowly changing into the azo-acid, nearly insoluble in cold alcohol, more readily soluble in hot alcohol, still more readily in hot methyl alcohol, insoluble in ether. Nitric acid reacts with it in the same way as with the azo-acid. When heated with concentrated hydrochloric acid in sealed tubes at 100 — 115° , it partly dissolves with a violet colour. From the solution, a white crystalline substance separates after some time which is easily soluble in alcohol, dilute hydrochloric and nitric acids, and in concentrated sulphuric acid. Salts of the azo-acids crystallise out from the solution of the hydrazo-acids in alkalis, and these effloresce when exposed to the air. The sodium salt contains 12 mols. H_2O . J. W. L.

Synthesis of Phenoxycoumarin. By A. OGLIALORO (*Chem. Centr.*, 1887, 1164, from *Rend. Acc. Sc. Napoli* [2], **1**, 90—91).—The author has already shown that phenylcoumarin is formed by the action of sodium α -toluylate on salicaldehyde and acetic anhydride (*Abstr.*, 1880, 164), and phenoxycinnamic acid by the action of sodium phenylglycolate on benzaldehyde and acetic anhydride, (*Abstr.*, 1881, 276). By heating acetic anhydride (100 grams) salicylaldehyde (25 grams) and sodium phenylglycolate (40 grams) for eight

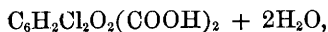
hours at 150—160° *phenoxy coumarin*, $C_{15}H_{10}O_3$, is formed. It crystallises in small, yellow prisms, melts at 113° (uncorr.), is nearly insoluble in cold, very sparingly soluble in hot water, more readily in alcohol, sparingly in ether and light petroleum, very readily in chloroform and benzene. An alkaline extract from the crude product of the reaction when acidified gave a brown precipitate that crystallised slowly. From this an acid, crystallising in yellow needles and melting at 175° with decomposition, could be separated, but has not yet been fully investigated. J. W. L.

Derivatives of Ethyl Quinoneparadicarboxylate. By A. HANTZSCH and A. ZECKENDORF (*Ber.*, **20**, 2796—2801).—The compound $C_{12}H_{12}Cl_2O_6$, obtained by the hydrogenation of ethyl dichloroquinonedicarboxylate (*Abstr.*, 1887, 727), was shown by Lehman, as quoted by the authors (*Ber.*, **20**, 1313), to exist in two forms. The first of these crystallises in colourless, radially grouped needles destitute of fluorescence, and melts at 123° to a green liquid; the second, formed from the preceding by rapid cooling of the fused substance, crystallises in greenish-yellow, dichroic tables which are stable at the ordinary temperature, but are very readily transformed by gentle heating into the original colourless needles. The former represents the stable modification, and is regarded as *ethyl dichloroquinoldicarboxylate*, $C_6(OH)_2Cl_2(COOEt)_2$, whilst the latter is the labile form, and is regarded as *ethyl dichloroquinonedihydrodicarboxylate*,



In the case of the compound $C_{12}H_{14}O_6$, from which the compound $C_{12}H_{12}Cl_2O_6$ is derived by chlorination and hydrogenation, the order is reversed, ethyl quinonedihydrodicarboxylate, the coloured compound, being the stable and ethyl quinoldicarboxylate, which is colourless, the labile form (*ibid.*). It is now shown that the dichloro-acid corresponding with these salts also exists in two modifications—one coloured and the other colourless.

When colourless ethyl dichloroquinoldicarboxylate is treated in the cold with concentrated aqueous soda, a greenish-yellow sodium salt is obtained. In aqueous solution, this also is greenish-yellow, and yields the unaltered ethyl salt on treatment with hydrochloric acid. If, however, the alkaline solution is saponified on a water-bath, evaporated nearly to dryness, and the sparingly soluble residue dissolved in water and acidified, a pale yellow solution is obtained which by rapid evaporation yields *dichloroquinonedihydrodicarboxylic acid*,



in the form of greenish-yellow needles. These are stable in the air, but effloresce on exposure over sulphuric acid, yielding *dichloroquinoldicarboxylic acid*; the stable form, is a white, anhydrous powder, which on heating carbonises without fusion or change of colour, is sparingly soluble in alcohol and ether, almost insoluble in water, and passes into the labile form only by heating with aqueous soda and acidifying the solution, since it does not directly combine with the elements of water.

Hitherto compounds of this type have been known to react as if they possessed only one of the two formulæ ascribed to them. An examination of ethyl tetrahydroxyterephthalate (Abstr., 1886, 1028) shows, however, that it sometimes reacts as if it were this compound, and at others as if it had the composition of the yellow, stable ethyl dihydroxyquinonedihydrodicarboxylate, $C_6H_2(OH)_2O_2(COOEt)_2$. Thus, when heated with acetic anhydride, it is converted into a *tetracetyl*-derivative, $C_6(OAc)_4(COOEt)_2$, a white, microcrystalline powder melting at 202° . If, however, the yellow salt is dissolved in concentrated aqueous ammonia and treated with hydroxylamine, it yields the *dioxime* of ethyl dihydroxyquinonedihydrodicarboxylate, $C_6H_2(OH)_2(NO_2)_2(COOEt)_2$, as a yellow powder melting at 156 – 157° without decomposition, and soluble in alkalis and ammonia. The very similar yellow, stable ethyl quinonedihydrodicarboxylate, on the contrary, does not react with hydroxylamine under the conditions just stated, but yields a colourless *diacetyl*-derivative of ethyl dihydroxyterephthalate when heated with acetic anhydride. Moreover, the compound $C_6H_2O_4(COOEt)_2$ (Abstr., 1886, 354) reacts as if it were ethyl dihydroxyquinonedihydrodicarboxylate, since it yields with hydroxylamine the *dioxime*, $C_6(OH)_2(NO_2)_2(COOEt)_2$; this is a yellow powder, which melts at 160° with decomposition, and is very sparingly soluble in alcohol and ether, soluble in hot chloroform and acetic acid.

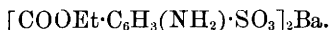
When ethyl succinosuccinate is treated with bromine in molecular proportion, and particularly when the bromination proceeds rapidly, a compound which crystallises in yellow needles is present in the mother-liquor from ethyl quinonedihydrodicarboxylate. This is a *hydrate* of ethyl quinonedihydrodicarboxylate, $C_{12}H_{11}O_8 + 2H_2O$. It melts at 113° , and is slowly converted into the anhydrous compound by recrystallisation, or more rapidly by boiling its alcoholic solution. In its fluorescence, colour reactions with ferric chloride, &c., it resembles the anhydrous salt, but differs from it by yielding, on treatment with hydroxylamine in ammoniacal solution, *ethyl quinoltetrahydrodicarboxylate*, $C_6(OH)_2H_6(COOEt)_2$, a yellow, crystalline substance melting at 128° .

W. P. W.

Preparation of Orthosulphobenzoic Acid. By N. R. BRACKETT and C. W. HAYES (*Amer. Chem. J.*, 9, 399–406).—The preparation of orthotoluenesulphonic acid from paranitrotoluene by the diazo-reaction is not satisfactory, as the greater portion is converted into an ethoxy-compound. Haller's method (decomposition of the hydrazine compound by copper sulphate) is much better. *Hydrazine orthotoluenesulphonic acid*, $N_2H_3 \cdot C_6H_3Me \cdot SO_3H$, prepared by the usual methods, crystallises in scales, is soluble in hot water, and has acid properties. With copper sulphate, it decomposes readily, but the orthotoluenesulphonic acid is not easily purified, and is not readily oxidised by potassium permanganate except in alkaline solution; moreover the yield of the benzoic acid is not satisfactory. Again, sodium orthotoluenesulphonate as prepared above does not give a good yield of orthotoluenesulphonamide, and this last when oxidised gives a fair yield of the sulphinide, but little of orthosulphobenzoic acid.

The best and quickest method of preparing this compound is that of Noyes (Abstr., 1886, 804) by the action of chlorosulphonic acid on toluene; a mixture of the para- and ortho-compounds is obtained which is best converted by ammonium carbonate into the toluene-sulphonamides; by treatment with potassium permanganate the para-compound is oxidised to parasulphobenzoic acid, and is precipitated by addition of dilute hydrochloric acid, whilst from the filtrate strong hydrochloric acid throws down the orthobenzoic sulphinide. This may then be converted into orthosulphobenzoic acid by evaporating with hydrochloric acid; the residue is extracted with water, from which the substance separates in large rhombic crystals; $a : b : c = 0.5507 : 1 : 0.8121$. H. B.

Paramido-orthosulphobenzoic Acid. By W. A. HEDRICK (*Amer. Chem. J.*, **9**, 410—418).—Paranitro-orthotoluenesulphonic acid is oxidised by potassium permanganate in alkaline solution, and the paranitro-orthosulphobenzoic acid precipitated from the filtered and concentrated solution by hydrochloric acid. The reduction of the nitro-group is effected by ammonia and sulphuretted hydrogen; the yield of the pure amido-acid amounts to one-half the weight of the nitrotoluene used. The following salts are described: $[\text{COOH} \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{SO}_3]_2\text{Ba} + 5\text{H}_2\text{O}$; $\text{C}_7\text{H}_5\text{NSO}_3\text{Ba} + \text{H}_2\text{O}$; $\text{C}_7\text{H}_5\text{NSO}_3\text{Pb}$; and $\text{C}_7\text{H}_5\text{NSO}_3\text{Ag}_2$. The silver salt, when boiled with methyl iodide, and then with water and calcium carbonate, yields a compound, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{COO} \\ \text{SO}_3^- \end{smallmatrix} > \text{Ca}$, whilst ethyl iodide and barium carbonate yield a neutral salt,



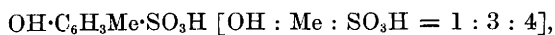
The free amido-acid has no basic properties, and no acetyl or benzoyl compound could be obtained from it.

Paradiazio-orthosulphobenzoic acid, $\text{COOH} \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{N}_2^- \\ \text{SO}_3^- \end{smallmatrix} >$, is best obtained by passing nitrous anhydride into a solution of the acid barium salt containing some of the same salt in suspension; it separates in white crystals. It may be converted into a well-crystallised hydrazine-compound in the usual way. The diazo-compound when boiled with water yields *hydroxysulphobenzoic acid*, of which the following salts are described:—

$[\text{COOH} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{SO}_3]_2\text{Ba}$, $(\text{C}_7\text{H}_3\text{SO}_6)_2\text{Ba}_3$, and $\text{C}_7\text{H}_4\text{SO}_6\text{Ca} + 5\text{H}_2\text{O}$; the last salt crystallises in the triclinic system; $a : b : c = 0.9567 : 1 : 1.0121$; observed faces: $\infty\bar{\text{P}}\infty$, $\infty\bar{\text{P}}\infty$, ∞P , and 0P .

H. B.

Metacresolsulphonic Acids. By A. CLAUS and J. KRAUSS (*Ber.*, **20**, 3089—3095).—*Metacresolparasulphonic acid*,



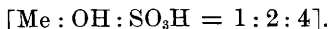
is obtained by heating sulphuric acid and cresol (equal weights) at 100 — 120° for some hours. The reaction also takes place at the ordinary temperature, but requires three or four days. It crystallises from dilute sulphuric acid in colourless plates (with 2 mols. H_2O)

melting at 75° (uncorr.), and from concentrated sulphuric acid in large, colourless plates (with $1\frac{1}{2}$ mol. H_2O) which melt at 95–96° (uncorr.). The anhydrous acid melts at 118°, and dissolves very readily in water, alcohol, ether, and benzene. The potassium salt (with $2\frac{1}{2}$ mols. H_2O) forms stellate groups of small crystals of a fatty lustre readily soluble in water; the sodium and lead salts are also readily soluble in water. The copper salt (with 3 mols. H_2O) crystallises in tufts of lustrous, pale-yellow prisms rather readily soluble in water. The sulphochloride, $C_7H_7O \cdot SO_2Cl$, forms a thin, honey-coloured syrup. The sulphonamide is readily soluble in alcohol and ether; it does not crystallise. When a dilute solution of the sulphonic acid is heated with chromic acid, toluquinone is formed.

Metacresoldisulphonic acid is prepared by heating metacresol with sulphuric acid (4 to 6 parts) at 120–140° for some hours, and forms an oily liquid readily soluble in water and alcohol, soluble in ether and benzene. The potassium salt crystallises with 3 mols. H_2O in colourless plates of a fatty lustre; the barium salt (with $\frac{1}{2}$ mol. H_2O) is very readily soluble; the lead salt is a readily soluble, slightly lustrous, crystalline powder. The copper salt is extremely soluble. The disulphochloride is a thick, honey-coloured liquid. The disulphonamide is also a syrup.

Metacresoltrisulphonic acid is formed when the cresol is heated with fuming sulphuric acid and phosphorus pentoxide at 180°. The barium salt is very readily soluble in water. N. H. M.

Orthocresolsulphonic Acids. By E. HANTKE (*Ber.*, 20, 3209–3213).—When orthocresol is heated with sulphuric acid for five to six hours on a water-bath, Engelhardt and Latschinoff's sulphonic acid (*Zeitsch. f. Chem.*, 1869, 621) is formed. The potassium salt crystallises with $\frac{1}{2}$ mol. H_2O . The acid has the constitution—



The same acid is formed together with Neville and Winther's sulphonic acid, $[Me : OH : SO_3H = 1 : 2 : 5]$ (*Ber.*, 13, 1946), when orthocresol is treated with sulphuric acid in the cold. The 1 : 2 : 5 acid forms deliquescent needles. N. H. M.

Synthesis of Anhydrides of Aromatic Sulphinic Acids. By R. OTTO and A. MILCH (*Ber.*, 20, 3337–3338).—In a previous paper (*Abstr.*, 1885, 1231), Otto and Rössing showed that when an alkyl chlorocarbonate is allowed to act on an alkaline sulphinate, an alkyl sulphinate and carbonic anhydride are formed. The authors now find that a similar reaction takes place when carbonic oxychloride is substituted for the chlorocarbonate. Phosgene gas and sodium benzene-sulphinate yield carbonic anhydride, sodium carbonate, and benzene-sulphinic anhydride, $(C_6H_5SO)_2O$. This compound is soluble in ether, but is decomposed immediately by water and alcohol, forming the acid or the ethyl salt respectively. L. T. T.

Sulphoneketones. By R. and W. OTTO (*J. pr. Chem.* [2], **36**, 401—432).—Phenylsulphonacetone behaves as a ketone, forming with sodium hydrogen sulphite colourless, tabular crystals of a double salt; with hydroxylamine, mono- or tri-clinic needles of *phenylsulphonacetoxime*, $\text{OH}\cdot\text{N}:\text{CMe}\cdot\text{CH}_2\cdot\text{SO}_2\text{Ph}$, melting at $147\text{--}148^\circ$; with ammonia, tabular crystals of *phenylsulphonacetoneamine*,



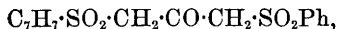
melting at $110\text{--}111^\circ$. With phenylhydrazine, it yields pale-yellow needles melting at 129° , of formula $\text{N}_2\text{HPh}:\text{CMe}\cdot\text{CH}_2\cdot\text{SO}_2\text{Ph}$, and with thiophenol it forms needles of *phenylsulphonacetone mercaptole*, $\text{CMe}(\text{SPh})_2\cdot\text{CH}_2\cdot\text{SO}_2\text{Ph}$, melting at $103\text{--}104^\circ$. When oxidised, it yields acetic acid, benzenesulphonic acid, and carbonic anhydride. When reduced by hydrogen in an acid solution, phenyl mercaptan and isopropyl alcohol are formed; in an alkaline solution, benzenesulphinic acid and isopropyl alcohol. With bromine, it yields *phenylsulphonebromacetone*, crystallising in colourless, silky needles, soluble in hot alcohol, and melting at 96° , and *phenylsulphonedibromacetone*, also in colourless needles, melting at $113\text{--}114^\circ$. With potassium hydroxide, it yields potassium acetate and methylphenylsulphone.

Diphenylsulphonacetone has the symmetrical constitution $\text{CO}(\text{CH}_2\cdot\text{SO}_2\text{Ph})_2$, for it is converted by potassium hydroxide into potassium phenylsulphonacetate and methylphenylsulphone. Diphenylsulphonacetoxime, $\text{OH}\cdot\text{N}:\text{C}(\text{CH}_2\cdot\text{SO}_2\text{Ph})_2$, obtained by heating the above compound with hydroxylamine hydrochloride, crystallises in rectangular tables melting at $136\text{--}137^\circ$. The phenylhydrazine compound forms yellow needles melting at 171° . With thiophenol, *diphenylsulphone mercaptan* is formed as a fine lustrous, crystalline powder, insoluble in water, melting at $190\text{--}191^\circ$.

A triphenylsulphone-derivative was not obtained by acting on phenyldibromacetone with sodium benzenesulphinate.

Paratolylsulphonacetone, $\text{COMe}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$, forms long, silky needles, soluble in alcohol, benzene, and chloroform, and melts at 51° . The bromo-derivative, $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$, crystallises in needles or rectangular plates, melts at $129\text{--}130^\circ$, and is sparingly soluble in hot water.

Diparatolylsulphonacetone, $\text{CO}(\text{CH}_2\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7)_2$, forms white, rhombic tables melting at 152° , soluble in hot glacial acetic acid and in chloroform. Paratolylsulphonephenylsulphonacetone,



prepared by the action of paratolylsulphonebromacetone on sodium benzenesulphinate, crystallises in rhombic plates and melts at 112° .

Calcium phenylsulphonacetate crystallises with $2\frac{1}{2}$ mols. H_2O in small needles, the lead salt with 2 mols. H_2O ; the silver salt when heated yields methylphenylsulphone and not diphenylsulphonacetone as was expected.

A. G. B.

Ethereal Salts of Benzoic Sulphinide. By R. N. BRACKETT (*Amer. Chem. J.*, **9**, 406—410).—The *methyl salt*, $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{NMe}$, CO

is obtained from methyl iodide and the potassium or silver salt. It crystallises from alcohol or hot water in flat needles melting at 131—132°. The *ethyl salt*, $C_7H_4SO_3NEt$, melting at 96—97° (Fahlberg and List give 93—94°), is prepared in like manner; at the same time some ethyl orthosulphamine benzoate is formed. The propyl salt melts at 60—70°.

When benzoic sulphinide is treated with phosphorus pentachloride, and methyl alcohol added in the cold, a crystalline substance is precipitated, probably $C_6H_4 < \begin{smallmatrix} SO_2 \\ CCl_2 \end{smallmatrix} > NH$; when this is boiled with methyl alcohol, it dissolves, and the solution on cooling yields first crystals of an acid melting above 330°, and then crystals melting at 123—125°; the latter is the dimethyl ether, $C_6H_4 < \begin{smallmatrix} C(OMe)_2 \\ SO_2 \end{smallmatrix} > NH$, of Remsen and Palmer, and when boiled with water and barium carbonate yields the barium salt of benzoic sulphinide. H. B.

Aromatic Lead Compounds. By A. POLIS (*Ber.*, 20, 3331—3336).—The author has obtained lead tetraphenyl (Abstr., 1887, 572) in measurable crystals. These crystals are colourless prisms belonging to the tetragonal system; axial ratio $a : c = 1 : 0.3808$. The corresponding tin compound gives $a : c = 1 : 0.38935$. Silicon tetraphenyl gives $a : c = 1 : 0.43969$. The three compounds are isomorphous, the value of the principle axis decreasing with the increase of atomic weight of the grouping element. *Lead diphenyl dichloride*, $PbPh_2Cl_2$, is formed by the action of chlorine on a carbon bisulphide solution of lead tetraphenyl or from the nitrate (*loc. cit.*) by precipitation with potassium chloride. It is a white powder, insoluble in alcohol and ether, sparingly soluble in chloroform, benzene, and carbon bisulphide. The *oxide*, $PbPh_2O$, obtained by the action of soda on an aqueous solution of the nitrate, is a white powder which does not fuse without decomposition. It does not seem to form a hydroxide, but is strongly basic in character, and dissolves in acids to form salts. The *acetate*, $PbPh_2(OAc)_2 + 2H_2O$, forms long, colourless needles; the *formate*, $PbPh_2(CHO_2)_2 + H_2O$, colourless needles; the *basic cyanide*, $PbPh_2Cy \cdot OH$, a white powder; the *thiocyanate*, $PbPh_2(CNS)_2$, and the *phosphate*, $(PbPh_2)_2P_2O_8$, white, flocculent precipitates; the *basic carbonate*, $(PbPh_2 \cdot OH)_2CO_3$, a white powder, and the *chromate*, $PbPh_2CrO_4$, a yellow precipitate which, when crystallised from a mixture of alcohol and benzene, yields yellowish crystals.

L. T. T.

Methylketole. By E. FISCHER (*Annalen*, 242, 372—383).—Many of the compounds mentioned in this paper have been previously described by the author (Abstr., 1887, 265). *Benzylidenemethylketole*, $CHPh(C_6H_5N)_2$, begins to melt at 242°, and melts completely at 246—247°. In the crystalline state this substance is sparingly soluble in the ordinary solvents, with the exception of acetone. The amorphous precipitate which is formed when water is added to the solution in acetone is freely soluble in ether and alcohol, but it soon changes to

the less soluble form. On oxidation, dimethylrosindole is produced (Abstr., 1887, 588).

Metanitrobenzaldehyde and methylketole readily unite, forming *metanitrobenzylidenemethylketole*. This substance is soluble in acetone, melts at 263° , and yields a red colouring matter on oxidation. When reduced with zinc-dust and ammonia it is converted into *metamido-benzylidenemethylketole*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_5\text{N})_2$. This base is soluble in ether, alcohol, and benzene. The preparation of *ethylidenemethylketole*, $\text{CHMe}(\text{C}_6\text{H}_5\text{N})_2$, from paraldehyde, zinc chloride, and methylketole has already been described (Abstr., 1887, 265). It melts at 191° , and boils with slight decomposition. It is freely soluble in alcohol, ether, and acetone.

By acting on methylketole and phthalic anhydride with zinc chloride at 100° , a compound of the composition $\text{C}_{17}\text{H}_{13}\text{NO}_3$ is obtained. It forms colourless prisms and dissolves in hot alcohol and acetic acid. The acid melts above 200° , and completely decomposes at a higher temperature. The author is of opinion that the acid may have the formula $\text{C}_6\text{H}_5\text{N}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$.

In the presence of zinc chloride, 1'-methylindole and phthalic anhydride unite to form phthalylmethylindole, $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_2$. The new compound crystallises in prisms, melts at 300° , and dissolves in hot acetone.

W. C. W.

Azo- and Amido-derivatives of Methylketole. By P. WAGNER (*Annalen*, **242**, 383—388).—The preparation of methylketoleazo-benzene, $\text{C}_6\text{H}_5\text{N}(\text{Me})\text{N}_2\text{Ph}$, has been already described (Abstr., 1887, 265). The compound is soluble in alcohol, ether, and benzene. On reducing the alcoholic solution with tin and hydrochloric acid, aniline and amidomethylketole are formed. The ketole crystallises in plates and melts at $112\text{--}113^{\circ}$. It is soluble in alcohol, ether, chloroform, and light petroleum. The hydrochloride crystallises in prisms, which turn pink on exposure to the air. When reduced with zinc-dust and hydrochloric acid, amidomethylketole yields first methylketole and then hydromethylketole. On oxidation with ferric chloride, amidomethylketole yields a mixture of two compounds, one of which is very soluble in alcohol. The other is less soluble in alcohol, crystallises in plates, and has the empirical formula $\text{C}_6\text{H}_7\text{NO}$. It melts at 225° with partial decomposition.

When dry hydrogen iodide is passed into an ethereal solution of methylketole, an amorphous precipitate ($\text{C}_6\text{H}_9\text{N}\cdot\text{HI}$) is produced. The compound is decomposed by water into its two components.

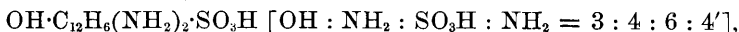
W. C. W.

Derivatives of β -Naphthindole. By A. STECHE (*Annalen*, **242**, 367—371).— β -Naphthylhydrazinelevulinic acid is deposited as a crystalline precipitate on the addition of water to an alcoholic solution of levulinic acid and β -naphthylhydrazine in their molecular proportions. At 170° , the acid is converted into the *anhydride*. This substance melts at 119° , and is deposited from hot alcohol in needle-shaped crystals. *Ethyl naphthylhydrazinelevulinate* is formed by the direct union of ethyl levulinate with β -naphthylhydrazine. It is crystalline, and melts at $129\text{--}130^{\circ}$. It is converted into methyl- β -

naphthindolacetic acid, $C_{10}H_6<\overset{NH}{CMe}>C\cdot COOH$, by the action of zinc chloride at 130—135°. This acid is freely soluble in alcohol, ether, acetone, and acetic acid. The silver salt is decomposed by boiling in water, forming a metallic mirror.

The acid decomposes at 210°, yielding carbonic anhydride and *dimethyl-β-naphthindole*, $C_{12}NH_7Me_2$ [$Me_2 = 2'' : 3''$]. The latter compound melts at 126° and dissolves freely in alcohol and acetic acid. It yields a dark-red picrate and a crystalline nitrosamine, and gives a characteristic blue coloration with acetic acid and ferric chloride. On reduction with zinc-dust and hydrochloric acid, *hydrodimethyl-β-naphthindole* is produced. This base is an oily liquid, which turns red on oxidation. The platinochloride is crystalline and is decomposed by boiling water. W. C. W.

Hydroxydiphenyl Bases. By A. WEINBERG (*Ber.*, 20, 3171—3178).—*Diamidohydroxydiphenylsulphonic acid*,



is prepared by reducing with stannous chloride, at a temperature not exceeding 30°, 300 grams of sodium benzene-azoparaphenolsulphonate dissolved in 500 c.c. of water. After 12 hours, the product is treated with hydrogen sulphide, filtered and evaporated to a small bulk; the *hydrochloride* of the sulphonic acid separates in large, clear crystals. The free sulphonic acid crystallises in needles from water, which dissolves it readily.

Diamidohydroxydiphenyl, $C_{12}H_7(NH_2)_2\cdot OH$ [= 4' : 4 : 3], is formed when diamidohydroxydiphenylsulphonic acid hydrochloride is heated with water at 180°. It crystallises in colourless plates melting at 185°, and is almost insoluble in water, readily soluble in dilute caustic alkali solutions. The alkaline solutions oxidise quickly when exposed to air. The hydrochloride is very readily soluble.

Diamidohydroxyphenyltolylsulphonic acid, $OH\cdot C_{12}H_5Me(NH_2)_2\cdot SO_3H$ [$NH_2 : Me : OH : NH_2 : SO_3H = 4' : 3' : 3 : 4 : 6$], is prepared from the dye obtained from orthotoluidine and paraphenolsulphonic acid. It crystallises in colourless needles which decompose when heated. It dissolves sparingly in water, readily in acids and alkalis.

Diamidohydroxyphenyltolyl, $NH_2\cdot C_6H_3Me\cdot C_6H_3(NH_2)\cdot OH$, prepared by heating the sulphonic acid with water at 180°, crystallises from water in lustrous plates melting at 177°; it dissolves readily in dilute aqueous potash, sparingly in ether and benzene. The *sulphate* is almost insoluble in water, more soluble in dilute acid.

Diamido-ethoxydiphenylsulphonic acid, $C_{12}H_{16}N_2SO_4$, is obtained by reducing sodium benzene-azophenetolsulphonate. It crystallises in needles sparingly soluble in cold water. The *hydrochloride* (with 2 mols. H_2O) is readily soluble.

Diamido-ethoxydiphenyl, $C_{14}H_{12}O(NH_2)_2$, is prepared by heating the above sulphonic acid with water at 170° for 8 to 10 hours; it forms flat, lustrous needles which melt at 134—135°, dissolves sparingly in water, ether, and benzene, readily in alcohol. When heated with hydrochloric acid, diamidohydroxydiphenyl (m. p. 185°) is formed.

The *sulphate* crystallises in prisms, sparingly soluble in water, readily in hydrochloric acid.

Diamido-ethoxyphenyltolylsulphonic acid is sparingly soluble in water. The *hydrochloride* forms large, prismatic crystals (with 4 mols. H_2O). The *barium salt* (with 8 mols. H_2O) crystallises in concentrically grouped needles.

Diamido-ethoxyphenyltolyl, $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}$, crystallises from water in flat needles melting at 117.5° ; it is sparingly soluble in water, cold alcohol, ether and benzene. When saponified, it yields diamido-hydroxyphenyltolyl melting at 177° .

Diamido-ethoxynaphthylphenyl, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_{10}\text{H}_5(\text{OEt})\cdot\text{NH}_2$

$[\text{NH}_2 : \text{C}_{12}\text{H}_{12}\text{NO} = 1 : 4; \text{C}_6\text{H}_4\cdot\text{NH}_2 : \text{OEt} : \text{NH}_2 = 1 : 3 : 4],$

is prepared by dissolving benzene-azo- β -naphthol in the equivalent amount of alcoholic potash, adding ethyl bromide, and boiling the whole for 24 hours under a slight pressure. When cold, it is filtered and evaporated down, when the benzene-azo- β -naphthyl-ethyl oxide remains as a dark-red oil. This is reduced with stannous chloride. The diamide melts at 72° , dissolves readily in alcohol, ether, and benzene; the alcoholic solution shows a greenish-blue, the ether and benzene solutions a violet fluorescence. The normal *sulphate* is sparingly soluble in water; the *hydrochloride* crystallises in needles of a silky lustre.

N. H. M.

Dinitrobenzidine. By E. v. BANDROWSKI (*Monatsh.*, **8**, 471—474).—By the hydrolysis of dinitrodiphenylparabenzidine with sulphuric acid at 130° , two *dinitrobenzidines* are produced together with phthalic acid. One modification less soluble in ammonia, forms long needles melting at 218 — 221° , and decomposing, when heated, with explosion. The more soluble modification forms saffron-yellow needles melting at 196 — 197° ; it is also distinguished from its isomeride by its greater solubility in alcohol and dilute acids. A dinitrobenzidine has previously been described by Strakosch, who obtained it by the nitration of acetylbenzidine; this has been shown by Brunner and Witt to be an ortho-derivative. From its method of formation, it would seem that this compound is identical with the isomeride melting at 218 — 221° described above, although Strakosch assigns a melting point of over 300° to the substance. However, the identity of the two substances is confirmed by the formation from both of them of the same tetramidodiphenyl.

V. H. V.

Bases produced by Nascent Formaldehyde. By J. TRÖGER (*J. pr. Chem.* [2], **36**, 225—245).—A crystalline, monacid base, probably $\text{CH}_2(\text{CH}:\text{N}\cdot\text{C}_6\text{H}_4\text{Me})_2$, is produced by the action of nascent formaldehyde on paratoluidine; it melts at 134° , dissolves in alcohol, ether, &c., but is insoluble in water; it forms a crystalline hydrochloride, sulphate, platinochloride, and picrate. When treated with nitrous acid, carbonic anhydride and nitric oxide are evolved, and a compound having the formula $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_2$ is formed; this substance dissolves in acetic acid, but is insoluble in alcohol, ether, water and

concentrated hydrochloric acid; it melts at 260—264° with decomposition, gives Liebermann's reaction, and also the nitric acid reaction with ferrous sulphate. A very similar product is obtained when the base is treated with nitric acid, nitrogen dioxide and carbonic anhydride being evolved; with acetic anhydride, it yields a very stable compound, $C_{42}H_{46}N_4O_5$.

Nascent formaldehyde and dimethylaniline yield tetramethyldiamidodiphenylmethane, from which a crystalline picrate and nitro-derivative, $CH_2[C_6H(NO_2)_3 \cdot NMe_2]_2$, were prepared.

Tetramethyldiamidodiphenylethane, $C_2H_4 \cdot (C_6H_4 \cdot NMe_2)_2$, is produced when dimethylaniline and carbon bisulphide are treated in alcoholic solution with zinc-dust and concentrated hydrochloric acid; it is a colourless, crystalline compound, melts at 87°, dissolves in ordinary solvents, but is insoluble in water; combines with methyl iodide, forms a crystalline picrate (melting at 190°) and platinochloride, and with nitric acid yields dinitronitrosodimethylaniline,



F. S. K.

Condensation Products from Paratoluidine and Paranitrobenzaldehyde. By A. BISCHLER (*Ber.*, 20, 3302—3306).—When paranitrobenzaldehyde, paratoluidine and concentrated hydrochloric acid are heated together in alcoholic solution, α -*paranitrophenyldiparamidotolylmethane*, $NO_2 \cdot C_6H_4 \cdot CH(C_6H_3Me \cdot NH_2)_2$, is formed. Crystallised from benzene, this substance forms white needles of the formula $3C_{21}H_{21}N_3O_2 + C_6H_6$, which lose their benzene at 110—120° and melt at 170—172°. It is but sparingly soluble in alcohol and ether, easily in boiling benzene. Its salts crystallise with difficulty, and are decomposed by water. The *platinochloride*, $C_{21}H_{21}N_3O_2 \cdot H_2PtCl_6$, forms yellow crystals soluble in boiling alcohol.

When, however, paranitrobenzaldehyde and paratoluidine are heated with strong sulphuric acid, an isomeric compound, β -*paranitrophenyldiparamidotolylmethane*, is formed. It crystallises in yellow scales melting at 126—127°, and is easily soluble in cold benzene and boiling alcohol or ether. It also is but a feeble base, but its salts are more easily crystallisable than those of the α -compound. The *hydrochloride* forms yellow needles, the *platinochloride* yellow scales.

The author believes the isomerism of these two compounds to be due to the benzaldehyde nucleus displacing ortho-hydrogen atoms in the toluidine in the α -case, meta-atoms in the β - (sulphuric acid) condensation.

L. T. T.

Compounds of Ketones with Dimethylaniline and Diethylaniline. By O. DÖBNER and G. PETSCHOW (*Annalen*, 242, 333—348).—The formation of tetramethyldiamidodiphenylpropane by the action of zinc chloride on acetone (1 mol.) and dimethylaniline (2 mols.), has been already described by Döbner (*Abstr.*, 1879, 787). By a similar reaction, *tetretthyldiamidodiphenylpropane*, $CMe_2(C_6H_4 \cdot NEt_2)_2$, has been prepared from diethylaniline and acetone. The base forms silky needles and melts at 76°. It is soluble in ether, carbon bisulphide, benzene, and light petroleum. The salts are very

soluble and crystallise with difficulty. The *hydriodide*, $C_{23}H_{34}N_2 \cdot 2HI$, forms pale-yellow plates, freely soluble in alcohol and in hot water.

Tetramethyldiamidotriphenylmethane is the chief product of the action of zinc chloride on acetophenone and dimethylaniline. Tetramethyldiamidodiphenylmethane and triphenylbenzene are also formed.

Tetramethyldiamidotriphenylethane, $CMePh(C_6H_4 \cdot NMe_2)_2$, is a pale-yellow oil, which gradually acquires a dark-red colour on exposure to the air. It boils above 360° with partial decomposition; under reduced pressure it may be distilled without undergoing any change. It is non-volatile in steam, and dissolves freely in ether, benzene, light petroleum and warm alcohol. The salts are very soluble in water and do not crystallise. It yields amorphous precipitates with the chlorides of gold, platinum, and mercury.

An acetic acid solution of the base turns blue on the addition of lead or manganese peroxide.

Benzophenone and dimethylaniline yield dimethyldiamidotriphenylmethane. Methyl hexyl ketone and dimethylaniline yield tetramethyldiamidodiphenylmethane and a liquid base, $C_{14}H_{23}N$, which is probably a hexyldimethylaniline. The chief product of the action of zinc chloride on diethyl ketone and dimethylaniline is tetramethyldiamidodiphenylmethane.

W. C. W.

Derivatives of Triphenylmethane. By U. ULLMANN (*J. pr. Chem.* [2], **36**, 246—272).—Diamido-derivatives of triphenylmethane are produced by the action of benzaldehyde on a mixture of a suitable aromatic base, and its hydrochloride. Aniline yields diamidotriphenylmethane; orthotoluidine gives *diamidorthotolylphenylmethane*, a white, microcrystalline powder whose melting point could not be determined.

Paratoluidine yields *diamidoparatolylphenylmethane* which crystallises from a mixture of benzene and light petroleum with $\frac{1}{2}$ mol. C_6H_6 , in concentric groups of yellow needles and melts at 185 — 186° ; it is a diacid amine, and forms a hydrochloride, picrate, &c. The colourless, crystalline *acetyl-derivative*, $C_{21}H_{18}(NHAc)_2$, melts at 217 — 218° ; the *benzoyl-derivative*, $C_{21}H_{16}(NHBz)_2$, melts at 196° . By means of the diazo-reaction, diamidoparatolylphenylmethane can be converted into the di-iodo-derivative $C_{21}H_{16}I_2$, crystallising in brownish-red prisms and melting at 167 — 168° . When distilled with zinc-dust, it yields paratoluidine and methylacridine, and, therefore, probably has the constitution $CHPh(C_6H_3Me \cdot NH_2)_2$ [$Me : CH : NH_2 = 1 : 3 : 4$]; from its formation by the above method, and as it can also be obtained by Mazzara's and by O. Fischer's methods, it follows that it is not necessary that the para-position with respect to the amido-group should be free in order to synthesise amidotriphenylmethane-derivatives.

In the preparation of the para-compound, a substance of the formula $C_{21}H_{16}N_2$ is also formed; it crystallises in long, nearly colourless needles, melts at 177 — 178° , and gives an orange-yellow, crystalline platinumchloride.

F. S. K.

Tetramethyldiamidothiobenzophenone. By O. BAITHER (*Ber.*, **20**, 3289—3298).—The author is inclined to think that this substance, which he previously described (*Abstr.*, 1887, 816), is really a thioketone, and identical with the compound obtained by Fehrmann (this vol., p. 156) from auramine. He believes the differences of properties and melting points are due to want of purity and difficulty in exactly determining the melting point. He now gives the melting point as 193—194°.

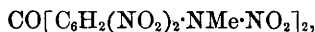
When the ketone is heated with benzoic chloride in carbon bisulphide solution, a *dichloro-derivative*, $\text{CCl}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, is formed, which is soluble in alcohol and glacial acetic acids, sparingly so in benzene and chloroform, and when heated decomposes. With water, it yields Michler's ketone, $\text{CO}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, and is probably the compound prepared from the latter in the manufacture of auramine colouring matters.

With benzoic chloride, the thioketone forms an *additive derivative*, $\text{CS}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{COPhCl}$. This substance is crystalline and melts below 200°, but was not obtained quite pure. It is soluble in acetic acid and in benzene. Alcohol and chloroform also dissolve it, but at the same time decompose it into its two constituents. Acetic chloride yields a similar derivative, $\text{CS}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{COMeCl}$, which is crystalline and begins to decompose at 160°. It is soluble in alcohol, acetic acid, chloroform, and benzene.

When the thioketone is heated with acetic anhydride and sodium acetate, it yields a compound, $\text{C}_{36}\text{H}_{48}\text{N}_4\text{O}_4\text{S}$, of which the constitution is probably $\text{S}[\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{OAc}]_2$. It forms a green powder which begins to decompose at 120°.

When heated with aniline, the thioketone appears to yield chiefly Michler's ketone, but with aniline hydrochloride it yields phenylauramine. The author found the melting point of the latter to be 170—171°. Phenylhydrazine appears to convert the thioketone into the corresponding oxy- (Michler's) ketone.

In his previous communication, the author described the product of the action of nitric acid on the thioketone as trinitrodimethylaniline. He now finds, however, that it is the same compound,



obtained from Michler's ketone. With hydroxylamine, this compound yields van Romburgh's compound, $\text{CO}[\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{NHMe}]_2$. It is probable that an oxime is first formed and is subsequently decomposed.

L. T. T.

Ring-formation with Elimination of Hydrogen Bromide or Nitrous Acid. By E. LELLMANN and O. SCHMIDT (*Ber.*, **20**, 3154—3157).—When β -naphthylamine is treated with glycerol, orthonitrophenol, and sulphuric acid, it yields β -naphthaquinoline in which the condensation has occurred at the 1:2 position; it was thought that by starting from α -bromo- β -naphthylamine, in which the 1 position is occupied, the condensation would occur at the 2:3 positions. α -Bromo- β -naphthylamine [$\text{Br}:\text{NH}_2=1:2$] was obtained by brominating β -acetonaphthalide; it was then treated with glycerol, orthonitrophenol, and sulphuric acid, and the product of the reaction crystallised

from light petroleum; it melted at 93.5° , and on examination it was found that β -naphthaquinoline had been formed with elimination of hydrogen bromide. α -Nitro- β -naphthylamine when treated in a similar manner yields the same compound with elimination of nitrous acid. The conclusion drawn is that the β' -carbon-atom is far less prone to ring-formation than the α -carbon-atom. The nitrophenol takes no part in the reaction, the result being the same whether it is present or not.

F. S. K.

Isomeric Naphthylaminesulphonic Acids. By G. SCHULTZ (*Ber.*, **20**, 3158—3162).—Bayer and Duisberg (this vol., p. 732) have stated that when β -naphthylamine is sulphonated, a mixture of sulpho-acids is obtained from which a hitherto unknown β -naphthylamine- δ -monosulphonic acid can be isolated; this compound yields a β -naphthol- δ -sulphonic acid which is identical with Casella and Co.'s naphtholsulphonic acid F; conversely, by heating this acid with ammonia, Bayer and Duisberg obtained a compound identical with β -naphthylamine- δ -sulphonic acid. Weinberg and Lange (this vol., p. 160) throw doubt on the identity of the acid which they themselves obtained from naphtholsulphonic acid F and that prepared by Bayer and Duisberg from β -naphthylamine. The author concludes that Weinberg obtained an impure product only, and gives proofs of the identity of the acids in question.

F. S. K.

Intramolecular Migration in β -Naphthylaminesulphonic Acids. By A. WEINBERG (*Ber.*, **20**, 3353—3355).—When β -naphthylamine- α - and γ -sulphonic acids are added to sulphuric acid (3 parts) previously heated at 160° , and the whole kept at this temperature for $1\frac{1}{2}$ hours, they both yield as chief product the 2:2' acid together with the 2:3' acid. The same product is formed by sulphonating β -naphthylamine sulphate. It is possible that Bayer and Duisberg's δ -acid (Abstr., 1887, 732) really consisted of this mixture. (Compare Schultz, preceding Abstract.)

N. H. M.

Conversion of Naphthylaminesulphonic Acid into Dichloronaphthalene. By H. ERDMANN (*Ber.*, **20**, 3185—3187).—When Witt's naphthalenedisulphonic acid (Abstr., 1886, 554) is diazotised, the product warmed with phosphorus pentachloride, and then distilled, dichloronaphthalene [1:4'] melting at 107° is obtained, together with some α -monochloronaphthalene. The yield of dichloronaphthalene is 30 to 40 per cent. of the theoretical.

N. H. M.

Action of Bromine on Diamido- α -naphthol. By T. ZINCKE and C. GERLAND (*Ber.*, **20**, 3216—3231; compare Abstr., 1887, 838).—When bromine acts on bromamido- α -naphthaquinonimide or bromohydroxynaphthaquinonimide, the main products are the tribromide, $C_{10}H_6Br_3NO_3$, and the dibromide, $C_9H_4Br_2O_2$; the latter melts at 176° , which is rather higher than the figure given by Kronfeld. In the second case, a small quantity of a third bromide melting at 130° is also formed.

By the bromination of bromamidonaphthaquinone or of bromohydroxynaphthaquinone, four brominated compounds are obtained, of which three are formed in very small quantity. Two of these are not yet worked out, the other is identified as the dibromide $C_6H_4Br_2O_2$. The main product is a dibromo-compound, $C_{10}H_6Br_2O_4$, *dibromotriketohydronaphthalene hydrate*, $C_6H_4<\begin{smallmatrix} CO \cdot C(OH)_2 \\ CO - CBr_2 \end{smallmatrix}>$; this crystallises in matted needles, melts at $114-115^\circ$ with decomposition, is readily soluble in alcohol, chloroform, and benzene, less readily in light petroleum, and is soluble in alkalis with yellow coloration. It is readily converted into bromoxy- α -naphthaquinone and hypobromous acid, either when heated alone or when boiled with benzene, toluene, dilute alcohol, or dilute acetic acid. When boiled with water, carbonic anhydride is evolved and a mixture of bromoxynaphthaquinone and the dibromide $C_6H_4Br_2O_2$ separates. When dissolved in ethyl or methyl alcohol and treated with hydrogen chloride, chlorohydroxy- α -naphthaquinone is formed. When boiled with aqueous potash, it yields a monobromo-compound, crystallising in small, nearly colourless plates and needles, and melting at $118-119^\circ$, and probably of the constitution $C_6H_4<\begin{smallmatrix} C(OH) \\ CO \end{smallmatrix}>CBr$ or $C_6H_4<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>CHBr$, probably due to the decomposition of an acid, $C_6H_4<\begin{smallmatrix} C(OH)(COOH) \\ CO \cdot CBr_2 \end{smallmatrix}>$, first formed, and for whose existence some evidence is adduced.

The corresponding dichloro-compound, $C_6H_4<\begin{smallmatrix} CO \cdot C(OH)_2 \\ CO - CCl_2 \end{smallmatrix}>$, prepared in similar manner, crystallises in thick, white needles, melts at 105° without decomposition, and is far more stable than the dibromo-compound. When treated with alkalis, it is converted into a crystalline compound melting at $128-129^\circ$, and if the alkaline solution is oxidised, small lustrous plates melting at $124-125^\circ$. The authors regard these substances as having the formulæ $C_6H_4<\begin{smallmatrix} C(OH)(COOH) \\ CO \end{smallmatrix}>$ and $C_6H_4<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>CCl_2$ respectively.

A chlorobromo-compound, $C_{10}H_6ClBrO_4$, was also prepared; it is less stable than the dichloro-compound, crystallises in white needles, melts at $104-105^\circ$, and when oxidised in alkaline solution yields plates of a substance melting at 141° .

When the dibromide $C_6H_4Br_2O_4$ is treated with aqueous soda, it yields bromoform, phthalic acid, and the monobromo-compound $C_6H_5BrO_2$ described above.

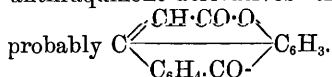
A. J. G.

Synthesis of Anthracoumarins from Cinnamic and Meta-hydroxybenzoic Acids. By S. v. KOSTANECKI (*Ber.*, 20, 3137-3145). When a mixture of cinnamic acid and metahydroxybenzoic acid, or any hydroxy-derivative of the latter, is heated with concentrated sulphuric acid, condensation products are formed.

From metahydroxybenzoic acid, *anthracoumarin*, $C_{16}H_8O_3$, is obtained as a yellow, crystalline compound melting at 260° ; it dissolves readily in hot glacial acetic acid, benzene, concentrated sulphuric acid,

and hot baryta-water, sparingly in alcohol; with boiling alkalis, it forms a yellow solution of green fluorescence which probably contains a salt of the corresponding coumaric acid. It is not dissolved by alkalis in the cold, whilst the compounds obtained from dihydroxybenzoic or gallic acid are readily soluble.

This fact shows that the hydroxyl-group has taken part in the condensation, and from the great similarity between these compounds and anthraquinone-derivatives the constitution of anthracoumarin is



In like manner *metahydroxyanthracoumarin*, $\text{C}_{16}\text{H}_8\text{O}_4$, is obtained from symmetrical dihydroxybenzoic acid. By sublimation or crystallisation from acetic acid, yellow needles are formed which melt at 325° and are only sparingly soluble in any ordinary solvent; they dissolve, however, in alkalis and sulphuric acid. When boiled with baryta-water, the coumarin-ring is probably split, an insoluble barium salt being precipitated. The yellow crystalline *monacetyl*-derivative, $\text{C}_{16}\text{H}_7\text{O}_4\text{Ac}$, melts at 255° .

Orthodihydroxyanthracoumarin, $\text{C}_{16}\text{H}_8\text{O}_5$, has already been obtained by Jacobsen and Julius (this vol., p. 56), who gave to it the name "styrogallol;" this compound and also its diacetyl-derivative were prepared, the latter melts at 260° , and its formation lends support to the constitution assigned to the anthracoumarins. Orthodihydroxyanthracoumarin can be fixed by a mordant, a fact which is in accordance with a theory put forward by the author (see this vol., p. 274).

F. S. K.

Purpurogallin. By S. C. HOOKER (*Ber.*, 20, 3259—3260).—The author recommends the following method of preparing purpurogallin:—20 grams of pyrogallol is dissolved in 330 c.c. of cold water and treated with a solution of 87 grams of potassium ferricyanide in 330 c.c. of water. Gas is evolved, the solution loses its deep red colour, and purpurogallin separates; in about $\frac{1}{2}$ hour the oxidation is complete. The yield is 13 to 14 per cent. of the pyrogallol employed.

Purpurogallin is formed in the oxidation of an aqueous solution of gallic acid by sodium nitrite.

Purpurogallin dissolved in sulphuric acid gives an intense, but fugitive, violet coloration when a trace of nitrous acid or a nitrite is added. The reaction is very characteristic and delicate.

A. J. G.

Hydrogenation of Aromatic Hydrocarbons. By E. BAMBERGER and W. LODTER (*Ber.*, 20, 3073—3078).—The hydrocarbons are boiled with amyl alcohol and sodium, the whole poured into water, and the upper layer dried with sodium carbonate and distilled. The yield varies with different hydrocarbons from 50 to 80 per cent. of the theoretical.

Tetrahydroretene, $\text{C}_{18}\text{H}_{22}$, forms a clear viscous oil which when kept from air remains liquid; in open vessels it solidifies, probably becoming oxidised to retene. It boils at 280° under 50 mm. pressure.

Tetrahydro-acenaphthene, $\text{C}_{12}\text{H}_{14}$, is a clear, colourless, viscous oil of

a slightly aromatic odour, boiling at 249.5° (corr.) under 719 mm. pressure.

Tetrahydrodiphenyl, $C_{12}H_{14}$, is a clear, colourless, viscous oil having a slight odour of diphenyl. It boils at 244.8° under 716 mm. pressure.

Dihydronaphthalene, dihydroanthracene (m. p. 108.5°), and tetrahydrophenanthrene were also prepared. N. H. M.

Sulphocamphylic Acid. By A. DAMSKY (*Ber.*, **20**, 2959—2967).—When ammonium sulphocamphylate is distilled with ammonium chloride, a yellowish-brown oil of peculiar turpentine-like odour is obtained, which, on fractionation, can be separated into two portions, one boiling at $108-110^{\circ}$ and the second at $195-196^{\circ}$. These were separately examined.

The fraction boiling at $108-110^{\circ}$ is a colourless, mobile liquid, having the odour of the crude product, and a sp. gr. = 0.7949 at 11.5° . It has the composition C_8H_{14} , and is a non-aromatic hydrocarbon, possibly identical with that obtained by Moitessier by distilling copper camphorate (*Jahresb.*, 1866, 410). On treatment with concentrated nitric acid, it is violently attacked and completely resinified, but when dissolved in acetic acid and treated with an acetic acid solution of nitric acid, no action occurs. Oxidation with chromic acid mixture does not convert it into an aromatic acid, and with permanganate it yields only oily fatty acids; whilst, contrary to the behaviour of aromatic hydrocarbons, it does not form an acid amide on treatment with amidoformic chloride. Bromine reacts with it readily, yielding an unstable, crystalline compound, $C_8H_{12}Br_2$, and subsequently liquid higher substitution-products, whilst the unstable, crystalline additive-compounds, $C_8H_{14}HCl$ and $C_8H_{14}HBr$, are formed when it is treated with hydrogen chloride and hydrogen bromide respectively.

The fraction boiling at $195-196^{\circ}$ undergoes slight decomposition at each distillation, and is a colourless liquid, having an odour similar to that of the lower fraction. It has probably the composition $C_{10}H_{14}O$, and forms oily compounds with hydroxylamine hydrochloride and phenylhydrazine hydrochloride; the *oxime* having probably the formula $C_{10}H_{14}:N\cdot OH$.

When potassium sulphocamphylate is fused with twice its weight of potassium hydroxide and the melt extracted with ether, a brown, resinous mass is obtained, which, on distillation in a vacuum, yields a pale-yellow, readily crystallisable oil. The crystals have the composition $C_9H_{12}O_2$, are readily soluble in alcohol and ether, very sparingly soluble in hot water and melt at 99° . The compound, although prepared by Kachler's method (*Abstr.*, 1874, 154), and having the same composition, differs from the substance prepared by him in its lower melting point and marked acid character. The *silver* salt, $(C_9H_{11}O_2)Ag$, is soluble in hot water; the *calcium* salt, $(C_9H_{11}O_2)_2Ca + 2H_2O$, forms yellowish crystals, soluble in hot water; the *barium* salt, $(C_9H_{11}O_2)_2Ba + 2H_2O$, is crystalline and soluble in hot water; the *methyl* salt was also prepared and is crystalline. Treated with bromine, the acid yields a crystalline compound with the evolution of

hydrogen bromide, and it is not reduced by the action of sodium amalgam. When distilled with soda-lime, it yields a yellow oil, which on rectification forms a colourless, mobile liquid of the composition C_8H_{12} , boiling at $133-135^\circ$, and polymerising on exposure to the air. W. P. W.

Action of Sulphuric Acid on Terebenthene. By J. BOURCHARDAT and J. LAFONT (*Compt. rend.*, **105**, 1177 — 1179). — The product of the gradual action of 467 grams of sulphuric acid on 9340 grams of French terebenthene boiling at $155-157^\circ$ (rotatory power -32.2°) was distilled in a current of steam; 79 grams of sulphuric acid remained in the free state, the rest having formed a compound $2C_{10}H_{16}, H_2SO_4$, which is almost though not quite fixed. This compound could not be isolated from the colophene with which it is mixed. It is a neutral substance and does not combine with potassium hydroxide. Alcoholic potash is without action in the cold, but at 150° decomposition takes place with formation of volatile products and the compound $C_{10}H_{16}, SO_2KH$, which crystallises from its aqueous solution in thin lamellæ.

The portion of the original product which distils with steam consists mainly of the unaltered hydrocarbon, without any camphene. The fraction boiling at $175-180^\circ$ has the composition $C_{10}H_{16}$, oxidises very readily, and is somewhat lighter than the original terebenthene. It absorbs hydrogen chloride readily yielding a liquid product, and when the latter is distilled in a vacuum, it yields cymene and terpinene hydrochloride, $C_{10}H_{16}, 2HCl$, melting at 48° . The rotatory power of the corresponding terpinene is only one-fifth or one-sixth that of another terpinene obtained from the same terebenthene by a different method.

The fraction boiling below 165° was treated successively four times with sulphuric acid, always with a similar result, but the fraction boiling at 157° , which gradually became smaller and smaller in quantity, diminished in rotatory power, and after a fifth treatment was converted into an easily solidified camphene. This camphene is formed by the decomposition of the small quantity of the sulphur compound which distils over with the water. This fraction, in fact, always contains a small quantity of free sulphuric acid.

When the original product, which is not volatile in steam, is heated at $200-250^\circ$, an energetic reaction takes place, water, sulphurous anhydride, and sulphur being produced. The liquid products contain a slightly active lævogryate compound boiling at 156° , cymene, terpinene, and dextrogryate camphenols. C. H. B.

Pimaric Acids. By A. VESTERBERG (*Ber.*, **20**, 3248—3253). — In a previous paper (Abstr., 1886, 1038) the author showed that the mother-liquor from the preparation of dextropimaric acid contained β -pimaric acid. From the very vigorous lævorotatory power of this acid, the name lævopimaric acid is now given to it; its separation and purification were attended with great difficulty. *Lævopimaric acid*, $C_{20}H_{30}O_2$, isomeric with dextropimaric acid, crystallises in the rhombic system; axial ratios, $a : b : c = 0.81042 : 1 : 0.61407$; ob-

served faces : ∞P , $\infty \bar{P}$, $P/2$, $2\bar{P}$, $0P$. It melts between 140° and 150° , and is insoluble in water, readily soluble in all the other usual solvents, its solubility being greater than that of the dextro-acid. One part of the acid dissolves in 10·8 parts of 98 per cent. alcohol at 15° . A solution of 3·174 parts of lævopimaric acid in 100 c.c. of alcohol has a lævorotatory power $[\alpha]_D = -272^\circ$. It forms readily crystallisable salts, of which the sodium, ammonium, and lead salts are described.

The author considers it very probable that Calliot's pyromaric acid (this Journal, 1874, 457) is a mixture of dextro- and lævo-pimaric acids.

A. J. G.

Action of Phenylhydrazine on Santonin. By C. GRASSI (*Chem. Centr.*, 1887, 1163—1164; from *Rend. R. Acc. Lincei* [4], 3, 521—522).—When a solution of santonin (10 grams) is heated with phenylhydrazine (10 grams) in acetic acid solution (sp. gr. 1·06), a yellow *hydrazide*, $C_{16}H_{16}O_2 \cdot N_2HPh$, separates, which melts at 220° , and is not decomposed by acids. Hydrochloric acid dissolves it in the cold with a reddish-yellow colour; on heating, a scarlet precipitate is formed. The hydrazine compound yields a platinumchloride.

J. W. L.

Lakmoïd and Litmin. By W. N. HARTLEY (*Proc. R. Dublin Soc.*, 5, 159).—Lakmoïd (*Abstr.*, 1885, 143) is soluble in strong alcohol, insoluble in water. A solution in 50 per cent. alcohol retains its colour with but slight alteration for several months. Litmin is insoluble in strong alcohol, but soluble in spirit of 50 per cent.; the solution was bleached after a time although not exposed to bright light. The photographic spectra of the two substances did not differ markedly. From these results, it follows that the two substances are not identical. Lakmoïd is a better reagent than litmin.

A. J. G.

New Brazilin-derivative. By C. SCHALL and C. DRALLE (*Ber.*, 20, 3365—3366).—*Tetramethylbrazileïn*, $C_{16}H_{10}O_5Me_4$, is prepared by mixing 2·7 grams of brazilin with 0·8 gram of sodium (each dissolved in alcohol); 8 grams of methyl iodide is then added, and the whole warmed on a water-bath until the colour changes to a yellowish-brown. The greater portion of the alcohol is distilled off and the rest evaporated on a water-bath. It is washed with water, dissolved in ether, and washed with dilute aqueous soda. It forms a brittle, transparent, amber-coloured mass which becomes crystalline when ether is poured over it. When crystallised from alcohol, it is obtained in colourless crystals melting at 138 — 139° . The compound has the properties of a phenol alkyl ether; it does not change when exposed to air, and yields an additive product with ammonia.

N. H. M.

Metanitroquinoline. By A. CLAUS and A. STIEBEL (*Ber.*, 20, 3095—3097).—*Metanitroquinoline*, $C_9NH_6 \cdot NO_2$, is prepared from 10 grams of nitraniline, 2·6 grams of picric acid, 14 grams of glycerol, and 14 grams of sulphuric acid. The mixture is afterwards boiled for some hours. The product after being freed from resin, is treated with light petroleum to remove the phenanthroline, which is also formed in

the reaction, and recrystallised from alcohol or water. It forms long, thin, colourless needles, melting at 131.5° (uncorr.). The *hydrochloride* crystallises in long, yellowish-white needles, melts at 225° with evolution of gas, and decomposes in contact with water. The *nitrate* crystallises in long, flat needles of a satiny lustre, not very readily soluble in water. The *platinochloride* forms large, amber-coloured prismatic crystals. *Metamidoquinoline*, $C_9NH_6NH_2$, prepared by reducing the nitro-compound with stannous chloride, forms long, hair-like, yellowish needles which melt at 186° (uncorr.); it is readily soluble in ether, chloroform, &c. When heated, it yields a sublimate of splendid red needles. It does not distil with steam. (Compare Abstr., 1887, 810). N. H. M.

Constitution of Quinoline-derivatives. By J. FREYDL (*Monatsh.*, **8**, 580—583).—The so-called β -amidoquinoline on conversion into the corresponding diazo-chloride and treatment of the same with potassium cyanide, yields a cyanoquinoline identical with the meta-cyanoquinoline of Bedall and Fischer. On hydrolysis, this nitrile yields a quinolinecarboxylic acid, identical with that obtained from an amidobenzoic acid by Skraup's reaction. The amidoquinoline is also converted by the diazo-reaction into a chloroquinoline, identical with the compound obtained by La Coste (Abstr., 1886, 159) from metachloraniline by Skraup's reaction. Then in the above group the substituted groupings are in the 2 position as derived from the 1 : 3 benzenoid derivatives. V. H. V.

Sulphonation of Quinoline. By G. V. GEORGIEVICS (*Monatsh.*, **8**, 577—579).—By the sulphonation of quinoline with Nordhausen acid, La Coste, as also Bedall and O. Fischer, obtained a mixture of the 1 : 2 and 1 : 3 quinolinesulphonic acids, the proportion of each which is formed being dependent on the conditions of the experiment. It is here shown that if the sulphonation is effected with ordinary sulphuric acid, the 1 : 4 sulphonic acid is produced, a result confirmed by the conversion of the acid into the corresponding nitrile and carboxylic acid. V. H. V.

Quinoline. By E. LELLMANN and G. LANGE (*Ber.*, **20**, 3084—3089; compare Abstr., 1887, 737).—Calcium parabromobenzenesulphonate crystallises in well-formed, monoclinic crystals with 2 mols. H_2O : $a : b : c = 0.5872 : 1 : 0.5168$; $\beta = 85^{\circ} 14' 42''$ (compare Goslich, this Journal, 1876, i, 929). Parabromometamidobenzenesulphonic acid crystallises in well-formed prisms with 1 mol. H_2O (not $1\frac{1}{2}$ mol. H_2O , Goslich, *loc. cit.*).

Orthobromoquinoline- α -sulphonic acid, $C_9NH_6BrSO_3H$ [$Br : SO_3H = 1 : 4$], is prepared by heating 5 grams of parabromometamidobenzene-sulphonic acid, 6 to 7 grams of orthonitrophenol, 20 grams of glycerol, and 25 to 27 grams of sulphuric acid in a reflux apparatus at 155 — 160° for six hours. The product is treated with water, steam-distilled, treated with baryta, filtered, and the filtrate boiled with animal charcoal. By precipitating the barium as exactly as possible with sulphuric acid and carefully evaporating the filtrate, the sulphonic acid

is obtained in small, lustrous plates with 1 mol. H_2O . The *calcium salt* with $6\frac{1}{2}$ mols. H_2O crystallises in long needles, readily soluble in water.

Tetrahydroquinoline-anasulphonic acid, $\text{C}_9\text{NH}_{10}\cdot\text{SO}_3\text{H} + \text{H}_2\text{O}$, is formed when 5 grams of bromoquinolinesulphonic acid is heated on a water-bath with concentrated hydrochloric acid and tin. It crystallises from dilute solutions in rhombic crystals; $a : b : c = 0.5041 : 1 : 0.7511$, and from concentrated solutions is monoclinic crystals; $a : b : c = 0.4855 : 1 : 0.5298$; $\beta = 55^\circ 10'$. When treated with oxidising agents, it shows the reactions characteristic of tetrahydroquinoline-derivatives.

The quinolinesulphonic acid previously prepared (*loc. cit.*) from metamidobenzenesulphonic acid, also yields a tetrahydroquinoline-sulphonic acid which completely resembles that just described.

N. H. M.

β -Quinolinedisulphonic Acid. By W. LA COSTE and F. VALEUR (*Ber.*, **20**, 3199—3201).— β -Quinolinedisulphonic acid, prepared by heating the pure barium salt with the necessary amount of sulphuric acid, crystallises in slender white needles, readily soluble in water, insoluble in alcohol, ether, benzene, and chloroform. (Compare *Abstr.*, 1887, 379.) The barium salt is obtained by treating the potassium salt with barium acetate. The potassium salt (with 1 mol. H_2O), is insoluble in alcohol, readily soluble in boiling water. When this salt is fused with 3 parts of potash at 160° , potassium β -hydroxyquinolinesulphonate is formed. *β -Hydroxyquinolinesulphonic acid* crystallises in yellow, lustrous plates, melting at 270 — 275° ; it dissolves readily in hot water, sparingly in alcohol, and still less in chloroform and carbon bisulphide.

β -Dihydroxyquinoline, $\text{C}_9\text{NH}_4(\text{OH})_2$, is prepared in a manner similar to the α -compound (*Abstr.*, 1886, 629), except that the temperature is only raised to 250 — 255° . It crystallises in slightly brown needles, readily soluble in ether, alcohol, benzene, chloroform, and carbon bisulphide, insoluble in water. It melts at 68° , and sublimes at a higher temperature in slender white needles. The salts are stable, but difficult to crystallise. (Compare also *Abstr.*, 1887, 973.)

N. H. M.

Tetrahydroquinaldine. By M. MÖLLER (*Annalen*, **242**, 313—321).—Tetrahydroquinaldine has already been described by Jackson (*Abstr.*, 1881, 742), and by Döbner and Miller (*Abstr.*, 1884, 183). The nitronitroso-compound, $\text{NO}_2\cdot\text{C}_{10}\text{NH}_{11}\cdot\text{NO}$, crystallises in golden plates, and melts at 152° . Methylhydroquinaldine, $\text{C}_{10}\text{H}_{12}\text{NMe}$, has been prepared by Döbner and Miller (*loc. cit.*). It can also be prepared by the action of tin and hydrochloric acid on quinaldine methiodide. *Methylhydroquinaldinemethiodide*, $\text{C}_{10}\text{NH}_{12}\text{Me}\cdot\text{MeI}$, crystallises in needles, melts at 205° , and dissolves freely in water and in hot alcohol. Freshly precipitated silver oxide converts it into the ammonium base, $\text{C}_{10}\text{NH}_{12}\text{Me}\cdot\text{MeOH}$, a crystalline, hygroscopic compound. The aurochloride crystallises in lemon-coloured needles, and the dichromate in six-sided plates. The platinochloride forms brick-red crystals, soluble in hot water. The base is decomposed by heat, yielding methyl, alcohol, and methyltetrahydroquinaldine

Ethyltetrahydroquinaldine, $C_{10}NH_{12}Et$, is a colourless liquid, boiling at 256° . The platinochloride and methiodide are crystalline. The latter melts at 187° and dissolves in water, but is not acted on by a solution of potassium hydroxide. W. C. W.

Quinaldine Alkyl Iodides. By M. MÖLLER (*Annalen*, **242**, 300—312).—Quinaldine methiodide and methylquinaldinium hydroxide have been previously described by Döbner (Abstr., 1884, 184), and by Bernthsen and Hess (Abstr., 1885, 558) respectively. In addition to the salts prepared by Bernthsen and Hess, the ammonium base yields an aurochloride, $C_{10}H_9NMeCl \cdot AuCl_3$, and a dichromate,



crystallising in lemon-coloured needles. The dichromate detonates at 90° . Ethylquinaldinium hydroxide on exposure to the air changes into a carmine-coloured resin. The platinochloride, $(C_{10}NH_9Et)_2PtCl_6$, is deposited from hot water in ruby prisms. The aurochloride,



forms golden needles. The dichromate detonates at 100° . *Quinaldine-propiodide* forms greenish-yellow prisms, soluble in water and in hot alcohol. It melts at 166 — 167° . The ammonium base is amorphous. It is soluble in alcohol and ether. The platinochloride, aurochloride, and dichromate are crystalline. *Quinaldine butiodide* is prepared by heating quinaldine with isobutyl iodide at 115° in molecule proportion. It crystallises in plates, and melts at 172° . The amyl iodide requires a temperature of 140 — 145° for its formation. It is crystalline, soluble in water and hot alcohol, and melts at 175° .

Orthomethylquinaldine methiodide is deposited from alcohol in yellow needles, and melts at 221° . The ammonium base is tolerably stable, and does not change rapidly on exposure to the air. The platinochloride, dichromate, and aurochloride are crystalline. The base is decomposed by heat, yielding orthomethylquinaldine. *Orthomethylquinaldine ethiodide* is deposited from alcohol in yellow needles, and melts at 228° . The ammonium base is a stable, oily liquid, and it forms crystalline platino- and auro-chlorides.

Paramethylquinaldine unites with methyl iodide at the ordinary temperature. The compound melts at 236 — 237° , and dissolves freely in water. The ammonium base is unstable. The platinochloride, dichromate, and aurochloride crystallise in needles. W. C. W.

Conversion of Indoles into Hydroquinolines. By E. FISCHER and A. STECHE (*Annalen*, **242**, 348—366).—In previous communications (Abstr., 1887, 588 and 976), the authors have described the conversion of methylketole into dimethyldihydroquinoline and dimethyltetrahydroquinoline, which are derivatives of β -methylquinoline. In the preparation of dimethyldihydroquinoline, a monomethyldihydroquinoline is formed as a bye-product. Dihydroethyldimethylquinoline and ethylmethylketole have already been described by the authors (*loc. cit.*).

Ethylmethyldihydroquinoline [Et : Me = 1' : 3'], prepared by the action of methyl iodide on ethylmethylketole and methyl alcohol at 120°, is a colourless oil which turns pink on exposure to the air. It boils at 254–255°, and forms salts which are freely soluble in alcohol and water. With ferric and platinic chlorides, it yields crystalline precipitates.

Trimethyldihydroquinoline, $C_9NH_6Me_3$ [1' : 3' : 4'], boils at 244°. The hydriodide crystallises in long prisms. The sulphate is precipitated from its alcoholic solution in crystalline scales on the addition of ether. The platinochloride is decomposed by boiling water.

The dimethyldihydro- β -naphthaquinoline, previously described by the authors (*loc. cit.*), is an imide base. The hydriodide and platinochloride are sparingly soluble in alcohol and in water.

The methiodides of the quinolines and dihydroquinolines are easily decomposed by alkalis, but the methiodides of the tetrahydroquinolines are not attacked.

Dihydroquinolines containing methylene in the indole-ring turn red on exposure to the air. W. C. W.

α -Alkylcinchonic Acids and α -Alkylquinolines. By O. DÖBNER (*Annalen*, **242**, 265–290).—The preparation of the α -alkylcinchonic acids and the properties of some of these compounds have already been described by the author (*Abstr.*, 1887, 504). In the preparation of α -isopropylcinchonic acid, a neutral substance of the composition $C_{19}H_{20}N_2O$ is obtained as a bye-product. It is insoluble in alkalis. α -Isopropylcinchonic acid, $C_9NH_5Pr^{\beta}\cdot COOH$ [2' : 4'], crystallises with $1\frac{1}{2}$ mols. H_2O . The hydrochloride, $C_{13}H_{13}NO_2\cdot HCl$, forms colourless plates, freely soluble in water. The platinochloride, which is abnormal $(C_{13}H_{13}NO_2\cdot HCl)_4\cdot PtCl_4 + H_2O$, and the aurochloride, $(C_{13}H_{13}NO_2)_2\cdot HAuCl_4$, are crystalline. α -Isopropylquinoline picrate is deposited from alcoholic solutions in yellow plates. It melts at 150°. The platinochloride crystallises with 2 mols. H_2O .

A neutral substance of the composition $C_{20}H_{22}N_2O$ is formed by the action of aniline on an ethereal solution of pyruvic acid and isovaleraldehyde. It crystallises from alcohol in silky needles, and melts at 160°. If a warm alcoholic solution is substituted for the ethereal solution, α -isobutylcinchonic acid is produced. The acid crystallises with $1\frac{1}{2}$ mols. H_2O . The hydrochloride, $C_{14}H_{15}NO_2\cdot HCl + H_2O$, crystallises in colourless plates, and dissolves freely in water. The platinochloride, $(C_{14}H_{15}NO_2)_2\cdot H_2PtCl_6$, is also crystalline. α -Isobutylquinoline picrate crystallises in plates, soluble in alcohol. It melts 161°.

On mixing together cold alcoholic or ethereal solutions of furfuraldehyde, pyruvic acid, and aniline, a neutral substance of the composition $C_{20}H_{16}N_2O_2$ is formed, but with warm alcoholic solutions, α -furfurcinchonic acid, $(C_4H_3OC_2NH_5)\cdot COOH$, is produced. This acid crystallises in greenish-yellow needles. It melts with decomposition between 210° and 215°, and dissolves freely in alcohol, ether, benzene, and in hot water. The silver, lead, and copper salts are sparingly soluble in water. The hydrochloride, nitrate, and

sulphate are freely soluble. The platinumchloride, $(C_{14}H_9NO_3)_2, H_2PtCl_6$, and the aurochloride, $(C_{14}H_9NO_3)_2, AuCl_3$, crystallise in needles. *α-Furfurquinoline* is obtained by heating furfureinonic acid at 300° . It melts at 92° , and boils above 300° . It crystallises in thick needles, and dissolves in alcohol, ether, and benzene. The platinumchloride, $(C_{13}H_9NO)_2, H_2PtCl_6 + 2H_2O$, and the aurochloride,

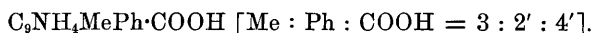


crystallise in needles, and dissolve in hot water. The dichromate forms orange-red needles. It is soluble in hot water. The dry salt decomposes at 100° . The picrate melts at 186° , and is deposited from hot alcohol in large yellow plates. W. C. W.

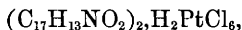
***α*-Phenylcinchonic Acid and its Homologues.** By O. DÖBNER and M. GIESEKE (*Annalen*, **242**, 290—300).—On mixing together ethereal solutions of aniline, pyruvic acid, and benzaldehyde, a compound of the composition $C_{22}H_{18}N_2O$ is obtained in the form of a crystalline mass, insoluble in acids, alkalis, and water. It melts at 225° , and dissolves freely in ether, benzene, acetic acid, and light petroleum. Strong acids and hot alkalis decompose the compound, yielding aniline and resinous products.

The preparation and properties of *α*-phenylcinchonic acid have been previously described by the authors (*Abstr.*, 1887, 504). The silver, lead, copper, and zinc salts were obtained in the form of amorphous precipitates.

A compound of the composition $C_{24}H_{22}N_2O$ is deposited in crystals on mixing ethereal solutions of paratoluidine, pyruvic acid, and benzaldehyde. It melts at 204 — 205° , and is insoluble in acids and alkalis. If warm alcoholic solutions are used, only a small quantity of this compound is formed, the chief product being *paramethyl-α-phenylcinchonic acid*,



This acid is deposited from alcohol in yellow needles. It melts at 228° , and is soluble in alcohol and ether. The platinumchloride,



forms golden needles. On distillation with soda-lime, paramethyl-phenylcinchonic acid yields paramethyl-*α*-phenylquinoline. *Orthomethyl-α-phenylcinchonic acid*, [1 : 2' : 4'], melts at 245° , and is freely soluble in ether and hot alcohol. The silver salt, $C_{17}H_{12}NO_2Ag + H_2O$, crystallises from hot water in needles. On distillation with lime, the acid yields *orthomethyl-α-phenylquinoline*. The base boils above 360° , and melts at 49 — 50° . W. C. W.

Parabenzoylquinaldine and Paradiquinaldine. By E. HINZ (*Annalen*, **242**, 321—329).—Paraldehyde acts on parabenzoylaniline dissolved in hydrochloric acid, forming *parabenzoylquinaldine*, C_9NH_4MeBz , and several bye-products. The new base melts at 67 — 68° ,

boils above 300° , and dissolves freely in hot water, alcohol, ether, benzene, chloroform, and light petroleum. The platinumchloride,



crystallises in needles, and is sparingly soluble in water. The anhydrous salt melts at $108\text{--}110^{\circ}$. The dichromate also crystallises in needles. The methiodide melts at 220° .

Diquinaldine is prepared by the action of paraldehyde on benzidine dissolved in hydrochloric acid. The yield is poor. *Diquinaldine*, $\text{C}_{20}\text{H}_{16}\text{N}_2$, melts at $206\text{--}207^{\circ}$, and dissolves in alcohol, benzene, chloroform, and acetone. It boils with slight decomposition above 360° .

The *platinumchloride*, $\text{C}_{20}\text{H}_{16}\text{N}_2, \text{H}_2\text{PtCl}_6 + 2\text{H}_2\text{O}$, is sparingly soluble in hot water. The nitrate, $\text{C}_{20}\text{H}_{16}\text{N}_2, 2\text{HNO}_3$, crystallises in needles, and is soluble in water. The dichromate is crystalline.

W. C. W.

Quinoline By E. BAMBERGER (*Ber.*, **20**, 3338—3344).—*Quinolinephenacyl bromide*, $\text{COPh}\cdot\text{CH}_2\cdot\text{C}_9\text{NH}_7\text{Br}$, is prepared by mixing equal mol. weights of quinoline and bromacetophenone dissolved in ether or in benzene; it separates in tufts of white needles. The yield is quantitative. It dissolves readily in alcohol and water, sparingly in ether and benzene, begins to decompose at $115\text{--}118^{\circ}$, and melts at about 165° . The *zincchloride* crystallises from water in small, thick, strongly refractive prisms; the nitrate crystallises in clear, strongly refractive prisms of a vitreous lustre, which are generally bent. The physiological action of the nitrate on mice, frogs, and cats is described; it resembles that of curare. When a quinolinephenacyl salt is treated with alkalis, the ammonium base is obtained together with a scarlet dye; the base forms white flakes, readily soluble in ether.

Formylphenacylanthrnic acid, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_2\cdot\text{COPh})\cdot\text{COH}$, is formed when 16 grams of potassium permanganate dissolved in 600 c.c. of water is gradually added to a cooled solution of 10 grams of quinolinephenacyl bromide in 1200 c.c. of water; after 12 hours, the colourless liquid is filtered, the manganese peroxide extracted several times with boiling water, and the collected filtrates from 50 grams of the phenacyl bromide evaporated down to 2 to 2.5 litres. It is then made acid, left for 24 hours in a cool place, and the crystals thus obtained are recrystallised from much water. It crystallises from dilute alcohol in white plates of a satiny lustre, melting at 184° , readily soluble in alcohol, less in hot water. Benzoic acid is formed as the chief product of the reaction. When the acid is boiled with dilute sulphuric acid, formic acid is obtained.

Pyridinephenacyl bromide, $\text{C}_5\text{NH}_5\text{Br}\cdot\text{CH}_2\cdot\text{COPh}$, prepared from pyridine and bromacetophenone, crystallises from a mixture of ether and alcohol in slender, lustrous, strongly refractive prisms. The *chromate* crystallises from water in lustrous, orange-coloured prisms; the *zincchloride* separates from its hot aqueous solution in lustrous, rhombic plates. When the bromide is treated with aqueous soda, it is decomposed into pyridine and benzoic acid.

N. H. M.

Acetic Tripiperide. By J. BUSZ and A. KÉKULÉ (*Ber.*, **20**, 3246—3248).—Ortho-amides, corresponding with the ortho-salts formed by acetic and other acids, have not yet been prepared. Experiments made with primary amines and with secondary amines of the type NHR'_2 , have failed to yield such compounds, but with secondary amines of the type NHR'' , of which piperidine is an example, success was attained.

Acetic tripiperide, $\text{CMe}(\text{C}_5\text{NH}_{10})_3$, is obtained by heating acetic trichloride (α -trichloroethane) for 4 to 5 hours in a reflux apparatus. It boils at 133 — 134° under 15 mm., or 261 — 263° under ordinary pressure. It is very stable, yielding but slight quantities of acetic acid when boiled for days with water or dilute acetic acid. The hydrochloride is crystalline and insoluble in ether; the platinochloride crystallises in golden-yellow plates.

Chloroform acts very slowly on piperidine, yielding a base boiling at 98° , which seems to be *orthoformic piperide*, $\text{CH}(\text{C}_5\text{NH}_{10})_3, \text{H}_2\text{O}$.

Benzoetrichloride reacts readily with piperidine, but whether a benzoic tripiperide is formed is not yet established. A. J. G.

Oxidation Products of Papaverine. By G. GOLDSCHNIEDT (*Monatsh.*, **8**, 510—528).—In continuation of former experiments on the oxidation of papaverine by potassium permanganate (*Abstr.*, 1886, 479), the author has more fully examined dimethoxycinchonic acid and other products formed. Papaverine hydrochloride yields oxalic, hemipinic, and veratric acids, which are contained in the filtrate from the reduced manganese peroxide; on treatment of this last with sulphurous acid, and extraction of the residue with hydrochloric acid, papaveraldine hydrochloride and dimethoxycinchonic acid are obtained, together with a substance of the formula $\text{C}_{10}\text{H}_9\text{NO}_4$. This last, named *hemipinisoimide*, to distinguish it from the isomeric hemipinimide obtained by Liebermann by the action of hydroxylamine on opianic acid, forms small, white needles melting above 300° ; it dissolves only on prolonged heating with alkali, but is at the same time decomposed into ammonia and hemipinic acid. It is also distinguished from hemipinimide by the unstable character of its potassium-derivative. The formula of this substance is discussed, but without satisfactory conclusions.

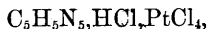
Dimethoxycinchonic acid, $\text{C}_9\text{NH}_4(\text{OMe})_2\cdot\text{COOH}$, crystallises with $2\text{H}_2\text{O}$ in small needles; it melts at 205° with violent evolution of carbonic anhydride, and formation of dimethoxyquinoline; it gives a brownish-red turbidity with ferric chloride, but no reaction with ferrous sulphate. Solutions of its salts give gelatinous precipitates with barium, calcium, copper, and silver salts. The *hydrochloride* crystallises with 2 mols. H_2O in glistening needles, and the *platinochloride* in groups of yellow needles. By hydriodic acid, the dimethoxy-acid is converted into *dihydroxycinchonic acid*, $\text{C}_9\text{NH}_4(\text{OH})_2\cdot\text{COOH}$, which is an amorphous powder, melting at 221° with violent evolution of gas. It gives a violet coloration with ferric chloride, and a reddish-yellow with ferrous sulphate. Its salts are all of a yellow colour, thus resembling those of hydroxycinchonic acid obtained by Weidel from the corresponding sulphonic acid.

Dimethoxyquinoline, $C_9NH_5(OMe)_2$, obtained by heating the dimethoxycinchonic acid, as also from papaveraldine when it is heated with alkali, forms a *hydrochloride* crystallising with $3H_2O$, a *picrate* crystallising in citron-yellow needles, and a *chromate* in small, orange-yellow, rhombic crystals.

This dimethoxyquinoline from papaverine is isomeric with that obtained from veratric acid; a list is given of the points of difference between the salts of these two bases. It is probable that in the methoxyquinoline from veratric acid, the methoxy-groups are in the position 1 : 2, but in that from papaverine the groups are in the positions 2 : 3; the author proposes to confirm this view by further experiments.

V. H. V.

Adenine. By A. KOSSE (Ber., 20, 3356—3358; compare Abstr., 1886, 556).—*Adenine nitrate*, $C_5H_5N_5.HNO_3 + \frac{1}{2}H_2O$, crystallises in stellate groups of needles; the dry salt dissolves in 110.6 parts of water. The *hydrochloride* (with $\frac{1}{2}$ mol. H_2O) forms transparent, monoclinic crystals, $a : b : c = 2.0794 : 1 : 1.8127$; $\beta = 61^\circ 40'$; the anhydrous salt dissolves in 41.9 parts of water. The *platinochloride*, $(C_5H_5N_5)_2.H_2PtCl_6$, crystallises from its dilute solution in needles; when a concentrated solution is boiled long, the *salt*,



separates as a bright yellow powder. The *silver compound*, $C_5H_4N_5Ag$, is obtained as an amorphous powder by adding an ammoniacal silver solution to a hot ammoniacal solution of adenine; with a large excess of silver solution, the compound $C_5H_4N_5.Ag_2O$ is formed. The *acetyl-derivative*, $C_5H_4N_5.Ac$, crystallises in small, white plates, readily soluble in hot water and alcohol, soluble in dilute acids and alkalis; it does not melt at 260° . The *benzoyl-derivative*, $C_5H_4N_5.Bz$, forms long, thin, lustrous needles, melting at 234 — 235° , readily soluble in hot alcohol, soluble in dilute acids and in ammonia.

Adenine is very stable towards acids, alkalis, and oxidising agents, but is readily reduced by zinc and hydrochloric acid, behaving like hypoxanthine.

N. H. M.

Ptomaines and Leucomaines. By A. GAUTIER (Bull. Soc. Chim., 48, 6—23).—A summary of our present knowledge concerning ptomaines, giving an account of the results obtained by the author, Brieger, and others, whose papers have from time to time appeared in Abstracts in this Journal (see Abstracts, 1881, 100, 224; 1882, 1115; 1884, 89, 188; 1885, 676; 1886, 634; also Bull. de l'Acad. de Med., 1886).

C. H. B.

Empirical Formula of Cholic Acid. By P. LATSCHINOFF (Ber., 20, 3274—3283).—Mylius has lately (Abstr., 1887, 982) upheld Strecker's formula $C_{26}H_{40}O_5$ for cholic acid, against this formula $C_{25}H_{42}O_5$ proposed by the author. The latter has therefore carefully re-examined this acid and its derivatives, with the result of confirming the formula $C_{25}H_{42}O_5$. He has been unable to obtain the acid perfectly anhydrous. Cholic acid crystallises in two forms (i) in tetrahydric

crystals, and (ii) in prismatic crystals. The first, obtained by crystallisation from alcohol, acetone, ether (of which it requires 510 parts at 18° for solution), isobutyl alcohol, or ethyl acetate, has the formula $C_{25}H_{42}O_5 + \frac{1}{4}H_2O$. It only loses this water of crystallisation at or above 145°, and partial decomposition always takes place simultaneously. Fusion ultimately results at 160—180°. The prismatic crystals, obtained by the precipitation of an acetic solution of the acid with water, have the formula $C_{25}H_{42}O_5 + H_2O$. They lose $\frac{3}{4}$ mol. H_2O at 120°, but the remaining $\frac{1}{4}$ is only lost at or above 145°. The author believes Mylius to have taken the not fully dehydrated acid as anhydrous. When this acid is dissolved in phenol, it forms white prisms, which give analytical results, agreeing with the formula $C_{25}H_{42}O_5 + \frac{1}{8}H_2O + \frac{7}{8}C_6H_6O$. It seems that the last trace of water is very firmly united to the cholic acid, and that when crystallised from other media with which it unites, the acid only takes up the complementary quantity of the medium. Thus the crystals from an alcoholic solution had the formula $C_{25}H_{42}O_5 + \frac{1}{8}H_2O + \frac{7}{8}C_6H_6O$.

Attempts to obtain mineral salts of the acid showed that here also a similar state of things existed. The salts all contained an excess of the base, that excess being, as in the case of the water of crystallisation, about one-eighth of an equivalent. With aniline and toluidine, however, cholic acid yields well-defined crystalline salts, which give numbers agreeing with those required by theory. *Aniline cholate*, $C_{25}H_{42}O_5 \cdot NH_2Ph$, forms needles melting at 140°; *metatoluidine cholate* needles melting at 140—180°.

L. T. T.

Action of Sodium Chloride in Dissolving Fibrin. By J. R. GREEN (*J. Physiol.*, **8**, 372—377).—When fibrin is extracted with a 5 or 10 per cent. solution of sodium chloride, a proteid goes into solution; on renewing this solution daily, removing that added on the previous day, it is found that in 32 to 35 days the whole of the fibrin is dissolved. In all these experiments, there was perfect freedom from putrefaction. When dissolved in this way, the fibrin is decomposed, with the formation of two globulins, one of which coagulates at 56°, is soluble in 1 per cent. sodium chloride solution, is readily converted into syntonin and alkali-albumin, and is not precipitated by weak acid; the other is insoluble in 1 per cent. sodium chloride solution, but soluble in a 10 per cent. solution; it coagulates on heating at 59—60°, is readily converted into alkali-albumin, but not into syntonin, the acid added for the latter purpose precipitating it, and in suspension it is not acted on. In some of its reactions, the former substance recalls the behaviour of fibrinogen, but neither corresponds with fibrinogen or serum globulin, and the latter cannot be made to re-form fibrin.

W. D. H.

Hæmatoporphyrin. By C. A. MACMUNN (*J. Physiol.*, **8**, 384—389).—A brownish pigment is scattered over several superficial portions of the mollusc *Solecurtus strigillatus*. On microscopical examination, it is found that, in the foot especially, the pigment is situated at the border of the cells, so that the boundaries between them are marked much in the same way that endothelium cells are

demonstrated by the use of silver nitrate. Granules in the cells contain the same pigment. Spectroscopic examination shows that the pigment is hæmatoporphyrin; this is identical with Moseley's polyperrythrin (*Quart. J. Mic. Science*, **17**, 1); the bands are identical with those seen in the pigment from the dorsal streak of the earthworm; a list of 12 other invertebrates in which the same pigment has been found is given. In many of these there is no hæmoglobin present, but the universal distribution of the histohæmatins, and the fact that these yield some of the decomposition products of hæmoglobin, fully explain the occasional appearance of a hæmoglobin-derivative in invertebrate animals (see Abstr., 1886, 638). W. D. H.

Physiological Chemistry.

Influence of Sleep on the Activity of Respiratory Combustion. By L. DE SAINT-MARTIN (*Compt. rend.*, 105, 1124—1128).—Experiments with doves show that, independently of the effect produced by fasting, natural sleep reduces the quantity of carbonic anhydride exhaled by about one-fifth, and reduces the quantity of oxygen absorbed by about one-tenth.

Experiments with dogs show that during sleep produced by morphine the proportion of carbonic anhydride exhaled falls to one-half the normal amount; during sleep produced by chloral or chloroform it falls to one-third the normal proportion.

When anaesthesia by chloroform is sufficiently long continued the blood becomes impoverished in oxygen and is charged with an amount of carbonic anhydride very considerably in excess of the normal proportion. In the early stage of insensibility, there is a diminution in the proportion of carbonic anhydride in the blood, but this is due to secondary causes.

C. H. B.

Coagulation of Fibrin and Intravascular Clotting. By F. KRÜGER (*Zeit. Biol.* 24, 189—225).—Wooldridge has shown that the phenomenon of coagulation is brought about by a substance which he calls A fibrinogen, obtainable from peptone plasma by simply cooling, and that the cellular elements which were hitherto considered essential, although they may assist coagulation, are nevertheless of secondary import. In his Croonian lecture he described coagulation as essentially similar to crystallisation. In plasma there are three constituents concerned in coagulation—A, B, and C fibrinogen. A and B fibrinogen are compounds of lecithin and proteid, and fibrin results from the transference of the lecithin from A fibrinogen to B fibrinogen. From this point of view the ferment is of secondary importance.

Wooldridge further found that a compound of lecithin and proteid closely allied to the A fibrinogen, which he considers probably the

precursor of A fibrinogen, exists in the testis and thymus gland of the calf, in the fluid of the lymph glands and the stromata of red blood-corpuscles. This compound is capable of causing widespread intravascular clotting in the entire absence of any cellular elements.

It is with reference to this last statement that the author joins issue. A large number of experiments have led him to the opposite conclusion, namely, that the corpuscular elements play the chief part in the coagulation, both within and without the body. He corroborates Wooldridge's statement, however, that the stromata of red blood corpuscles produce intravascular clotting.

The leucocytes obtained by centrifugalising the fluid of the lymph glands produce intravascular clotting, but the supernatant liquid, the author states, is inert, or almost so. He considers that any slight action of the fluid may be accounted for by the presence of some leucocytes, for he found it impossible to remove them completely, even by centrifugal action.

J. P. L.

Influence of Calcium Sulphate on the Coagulation of the Blood. By J. R. GREEN (*J. Physiol.*, 8, 354—371).—A saline extract of washed blood clot contains fibrin ferment (Buchanan). Heating such an extract nearly to the boiling point delays the action of the ferment but does not destroy it; the ash was found to contain a definite and fairly constant amount of calcium sulphate. A saturated solution of calcium sulphate was prepared, and on adding 1 c.c. of this to 10 c.c. of diluted magnesium sulphate plasma, coagulation set in with great rapidity; a very small amount of the salt (0.001 per cent.) has considerable clotting power; this increases with the quantity of calcium sulphate used, but not proportionately. In other experiments with peptone or leech extract, in which coagulation was retarded by cold, the addition of calcium sulphate caused it to take place in some cases very rapidly, in others more slowly.

Calcium sulphate cannot be regarded as the fibrin ferment however; addition of that salt to pericardial fluid or to a sodium chloride solution of fibrinogen causes no coagulation in those fluids; but when the ferment is present, addition of salt accelerates the coagulation.

The next point investigated was whether it is possible to have coagulation in the absence of calcium sulphate; peptone-plasma was dialysed for three days into a 0.6 per cent. solution of sodium chloride; if water had been used outside the membrane, the globulins of the plasma would have been precipitated. Dilution of the plasma with saline solutions then caused no clotting, nor did the passing of a stream of carbonic anhydride through the plasma coagulate it as it does ordinary peptone-plasma. But on adding a little calcium sulphate to the diluted plasma coagulation rapidly set in.

In plasma prevented from coagulating by cold, or by admixture with magnesium sulphate, similar experiments were performed, dialysis being carried out at the temperature of 1°. After a week's dialysis, dilution caused no coagulation, but after adding calcium sulphate clotting set in, though slowly. It was suggested that the fibrin ferment exists as a zymogen in plasma, and is converted into ferment by the action of calcium sulphate. Horse's blood kept from

clotting by cold was precipitated by a large excess of alcohol; after remaining for some weeks under the spirit, the precipitate was collected, dried, and extracted with a 0.6 per cent. sodium chloride solution; this was warmed with calcium sulphate for an hour, and then that salt removed by dialysis; but on diluting plasma or pericardial fluid with this there was no hastening of the coagulation; that is, there was no evidence of zymogen conversion.

Calcium sulphate helps the working of the ferment, but it is not concerned with its liberation. Quantitative experiments on the relation of the amount of fibrin formed to the amount of calcium sulphate added negative the idea that fibrin is a union of fibrin with that salt. Hammarsten (Maly's *Jahrsbericht*, 4, 135) has shown that calcium phosphate is necessary for the proper activity of the rennet ferment.

W. D. H.

Secretion of the Gall Bladder. By B. BIRCH and H. SPONG (*J. Physiol.*, 8, 378—383).—The fluid was obtained from two women in which a fistula remained in each case after the operation of cholecystotomy had been performed. A celluloid cannula was found to be the best to use, as it did not set up the irritation consequent on the use of metallic ones. About 20 c.c. in the day was collected, but it is supposed that a third or more of the fluid was lost. In both cases the bile channels were completely closed off from the gall bladder, and no biliary constituents were present. The fluid was therefore the secretion of the mucous membrane of the gall bladder, and in both cases it had identical composition and properties. Both patients were also in excellent health. The fluid was sometimes clear, sometimes faintly opalescent; it was viscid; its specific gravity varied from 1.011 to 1.012 at 12.5°. On microscopic examination, it was found to contain a few leucocytes. It was always distinctly alkaline, which reaction must be attributed to alkaline sodium phosphate. The following is the approximate quantitative analysis in parts per 1000:—

Water and gases	979.7
Solids.....	20.3

A. Organic—

Mucin.....	} 12.09
Proteid matter, a trace.....	

B. Inorganic—

Chlorine.....	3.84
Carbonic anhydride	0.29
Sodium (combined with Cl).....	2.50
Soda (combined with CO ₂)	0.41
Potassium salts and phosphates by difference	1.17
	<hr/> 20.30

The fluid has distinct diastatic properties, which were destroyed by boiling; the fermentation agent was not definitely separated; the

alcoholic precipitate, however, was found to contain it, whilst none remained in the filtrate; the ferment was also non-diffusible. Some was filtered through a porous cell; the filtrate was inoperative on starch, whilst the residue, which evidently represented the mucin that could not get through the filter, was still active. The fluid had no curdling action on milk, and no emulsion was formed when it was mixed with cod-liver oil. The secretion, moreover, does not readily putrefy, although it was demonstrated by means of experiments with sterilised peptone infusion that it has no active power in restraining putrefaction; its apparent immunity from change being due to its poverty in nourishing material. The secretion cannot be regarded as playing any important part in digestion, the small diastatic action it possesses being shared by many fluids in the economy on which it does not confer any special digestive value. Its use is no doubt confined to lubricating the walls of the gall bladder, and it adventitiously adds some mucus to the bile which comes to repose in it. W. D. H.

Analyses of American Fishes. By W. O. ATWATER (*Amer. Chem. J.*, 9, 421—452).—52 species of American fishes were examined. The methods of analysis are described, and tables are given containing proportion of edible portion and the amounts of nitrogen, proteids, ether extract, and ash of this portion of the fish. The composition varies very considerably, thus—

	Water.	Dry substance.	Albuminoid.	Fat.	Ash.
Mackerel	73·4	26·6	18·3	7·1	1·3
Haddock	81·7	18·3	16·8	0·25	1·2
Cod	82·6	17·4	15·8	0·4	1·2
Halibut	75·4	24·6	18·4	5·2	1·1
Salmon	63·6	36·4	21·6	13·4	1·4
Spent salmon, female	78·2	21·8	17·8	2·8	1·2

H. B.

Ferments in Normal Urine. By E. STADELMANN (*Zeit. Biol.*, 24, 226—260).—Very divergent opinions have from time to time been expressed with reference to the presence of ferments in normal urine. It may be safely said that all observers are agreed on the constant occurrence of pepsin in normal urine, but the most conflicting evidence is forthcoming as to the presence of trypsin.

Grützner and his pupils, Sahli, Gehrig, and Holovtschiner state that trypsin is a constant concomitant of normal urine, and that it is present in regular quantity. Mya and Belfanti state that both pepsin and trypsin are present in normal and pathological urine, except in cases of acute and chronic nephritis.

In opposition to this, Leo denies the occurrence of trypsin in all cases, but admits the presence of pepsin in normal and in most pathological cases. In cancer of the stomach and typhoid fever, pepsin, is however, absent.

In the present investigation, a complete survey of the whole subject has been undertaken. The occurrence of pepsin is further corroborated, but in no instance has trypsin been found. The author, therefore, considers with Leo that the apparent digestion of raw fibrin in alkaline urine, in Grützner's and other observers' experiments, was due to the presence of sepsis which had not been sufficiently guarded against. Raw fibrin does disintegrate in alkaline urine even in the presence of thymol, owing no doubt to the presence of bacteria in the raw fibrin, but in no instance did any digestion or disintegration take place when boiled fibrin was used. As the direct experiments with urine were negative, a large quantity was evaporated nearly to dryness at 40°, the residue thoroughly extracted, and washed with alcohol. The residue, which would contain any trypsin that might be present, was then dissolved in a small quantity of water and tested with regard to its digestive power, but the solution was found to be entirely inert. When proper precautions are taken to ensure the absence of any putrefactive change, the results are always negative.

Certain inorganic salts—potassium, sodium, and ammonium sulphates, and potassium and sodium phosphates—hinder tryptic digestion in a marked degree. This is especially the case with the potassium phosphates. J. P. L.

Physiological Action of Ethyl Lactate. By P. PELLACANI and G. BERTONI (*Chem. Centr.*, 1887, 1149; from *Arch. Ital. Biol.*, 7, 201--208).—The ethyl salt of fermentation lactic acid, when taken by the mouth in concentrated solutions, causes great irritation of the throat and the first parts of the alimentary tract. When subcutaneously injected it causes no local irritation. A 10 to 15 per cent. solution does not coagulate albumin. It is a liquid, and soluble in all proportions in water, alcohol, and ether. Its hypnotic properties are weak, and its physiological action is compared with that of chloral and iodal. When given in doses sufficient to cause deep anaesthesia, it causes death by interference with the respiration. W. D. H.

Physiological Action of Trimethylethylxyammonium and Trimethylvinylammonium Hydroxides. By V. CERVELLO (*Chem. Centr.*, 1887, 1150; from *Arch. Ital. Biol.*, 7, 232—233).—0.01 gram of the hydrochloride of the first base causes in the frog, dilatation of the pupil and increased frequency of respiration; after about two hours the animal returns to its normal condition. To cause complete paralysis, at least 0.05 gram must be given: death then occurs in about three hours. The pulse is but little affected. In a rabbit weighing 850 grams, 0.5 gram caused increased secretion of tears, running from the nose, and enlargement of the pupil. Paralysis, which ensues after large doses, is produced like that caused by curare. Aqueous solutions of trimethylvinylammonium hydroxide (neurine), cause the same symptoms, but its action is more powerful. The antagonism between this base and atropine holds only with regard to the heart and glandular system. Atropine will not prevent death after the administration of lethal doses of neurine. Neurine thus

resembles curare in its physiological action, and muscarin in its antagonism to atropine. W. D. H.

Physiological Action of "Saccharin." By V. ADUCCO and U. MOSO (*Chem. Centr.*, 1887, 1148—1149; *from Arch. Ital. Biol.*, **7**, 158—171; and **8**, 22—36).—"Saccharin" (Fahlberg) is but little soluble in cold water, but dissolves more easily in hot, and very easily in boiling water. The solution so obtained is strongly acid. On cooling the hot, concentrated aqueous solution, the substance separates in monoclinic (?) needles melting at about 200°. It is more easily soluble in ether, and still more so in alcohol: it dissolves easily in water if its solution be continuously and carefully neutralised, but is reprecipitated on addition of hydrochloric acid. Even in large doses, it is harmless to the animal organism. After its administration, the urine has a well-marked, sweet taste, and decomposes with much more difficulty; it contains unaltered saccharin. It causes no alteration in nutrition or metabolism, with the exception that the chlorides of the urine are increased in amount. Saccharin is not excreted by the saliva nor by the milk. Half an hour after its administration by the mouth, the urine acquires a very sweet taste, which after doses of 5 grams disappears in 24 hours. 0.16 gram of saccharin weakens the alcoholic fermentation of dextrose, as well at 30° as at 16°. A mixture of urine with an equal volume of a 0.32 per cent. solution of saccharin does not undergo the ammoniacal fermentation for over seven days, whilst urine mixed with a corresponding amount of salicylic acid ferments in less than that time. Saccharin also prevents putrefaction during pancreatic digestion. A percentage of 0.16 to 0.32 of saccharin hinders but does not prevent gastric digestion. A percentage of 0.0064 has no such effect. Benzoic acid in similar amounts has the same effect; salicylic acid a stronger effect. Saccharin hinders the amylolytic action of saliva, especially in a neutral solution, but not so much as does salicylic acid; benzoic acid, on the other hand, is not so active. As the sweetness of saccharin is 280 times greater than that of cane-sugar, it can be substituted for the latter in common use. The taste is pleasanter on neutralising and diluting. It can also be used to prevent fermentative changes in the stomach, in the urinary bladder, and for disinfection generally.

W. D. H.

Physiological Action of Santonin and its Derivatives. By F. COPPOLA (*Chem. Centr.*, 1887, 1206, 1208—1209, 1301—1302; *from Rend. R. Acc. Lincei* [4], **3**, 513—521, 573—578).—One per cent. solutions of santonin, of photosantonin, and of isophotosantonin in olive oil, at 38°, do not kill the ascarides lumbricoidi of the pig. Whilst, however, the two first-named substances increase the movements of the animal and cause convulsions, with isophotosantonin the reverse is the case. The other santonin-derivatives examined resemble the two first in their action on the worms. It was also found that doses of 1.25 grams of santonin daily administered to the pig did not kill the worms. The action of santonin on worms resembles its action on vertebrate animals. In order to lessen the toxic effects of

the drug on the animal to which it is given it is advisable to use santoninoxime (Cannizzaro, *Rend. R. Acc. Lincei*, 1885, 703) which is insoluble in water, easily soluble in oils and fats, but not in organic acids, nor is it acted on by the gastric juice. The increased activity of the worms leads to increased peristaltic action of the intestine, which thus voids them. In the urine, santoninoxime passes out slowly as santonin; it is less poisonous than santonin, but is equally efficacious in its action on the parasites.

Experiments were also performed in order to see whether the photo-santonin-derivatives differed in their action from that of santonin, and also to discover if any relation existed between physiological action and the power of solutions of these compounds to rotate the plane of polarised light. *Photosantonin acid*, $C_{15}H_{22}O_5$, has a narcotic action on frogs, doses of 0.02 to 0.03 gram abolishing first voluntary movement, then the movements of respiration; the heart and reflexes are but little affected: doses of 0.04—0.06 gram first diminish, and then abolish reflexes, and stop the heart in diastole. In vertebrate animals the action is similar, except that the reflexes are not affected. *Photosantonin*, $C_{17}H_{24}O_4$, acts in the same way, but on account of its smaller solubility the effects are not so marked. *Santonin*, $C_{15}H_{18}O_3$, itself, and sodium santonate cause as their chief symptoms convulsions; it seems then that the action of light is to modify the physiological action of these compounds on the nervous system; the action on the respiratory and circulatory systems is, however, the same. *Santonin acid*, $C_{15}H_{20}O_4$, in doses of 0.03 gram, causes no effect in frogs; 0.04 to 0.05 gram produces narcosis, abolishes respiratory movements, but does not lessen reflexes. Larger doses affect the reflexes and kill the animal; if the dose is not lethal, the animal experiences clonic convulsions like those produced by santonin, as the narcosis passes off. In a rabbit of 1 kiló. body-weight, doses of 1 to 1.5 gram applied hypodermically have no effect: 2 to 3 grams caused sleep in $\frac{1}{2}$ to 1 hour, and, like santonin, epileptic convulsions. There is no action on the circulation, except with lethal doses, which stop the heart in diastole: atropine does not antagonise this action; this acid thus produces the effect of santonin combined with that of the photo-compounds, both narcosis and convulsions. Santonic and isosantonin acids act like photosantonin acid. Isophotosantonin, $C_{17}H_{24}O_4$, is no hypnotic, but easily causes strong convulsions. Isophotosantonin acid, $C_{15}H_{22(4)}O_5$, acts similarly, but is weaker. The derivatives of santonin that cause convulsions do so by their action on the medulla, not on the spinal cord. The photo-derivatives contain, like santonin, a closed naphthalene nucleus, and the differences on their constitution are to be found in the side-chains. There was found to be no connection between physiological action and the direction or amount of rotation of the plane of polarised light.

W. D. H.

Physiological Action of Thallin. By G. PISENTI (*Chem. Centr.*, 1887, 1149—1150; from *Arch. Ital. Biol.*, 7, 134—141).—Jaksch (*Zeit. Klin. Med.*, 8) states that thallin is a strong febrifuge, but one which has no influence on the course of the disease. In the present research it was found that small doses (0.025—0.075 gram) lower the

temperature of fever patients directly and considerably, but only for a short time : and as Jaksch states, there is no alteration in the course of the malady which causes the high temperature. The salt used was the sulphate. This salt hinders putrefaction, lowers the blood pressure considerably, and leaves the body by the liver and kidneys. Subcutaneous injection is not dangerous. W. D. H.

Action of Brucine and Strychnine. By T. J. MAYS (*J. Physiol.*, **8**, 391—403).—It was found that in the frog the physiological effects of poisoning by strychnine and brucine respectively differ as follows :—(1.) Brucine primarily affects the posterior, whilst strychnine affects the anterior extremities. (2.) Convulsions appear very early in strychnine, and not at all or very late in brucine poisoning. (3.) Convulsions invariably develop before death occurs in strychnine poisoning, whilst death often occurs in brucine poisoning without a trace of spasm. (4.) Brucine diminishes sensibility when locally applied, whilst strychnine does not. (5.) The local anæsthetic effect of brucine appears to bear a direct relationship to its degree of freedom from strychnine. W. D. H.

Physiological Action of Caffeine. By F. COPPOLA (*Chem. Centr.*, 1887, 1209—1210; *from Ann. Chim. Farm.*, **8**, 10—38).—From the result of numerous experiments on both cold- and warm-blooded animals the following conclusions are drawn :—Caffeine does not belong to the same pharmacological group as digitalin, because it acts on the heart and the nerve-centres, whilst digitalin and the glucosides derived from it are characterised by their exclusive action on the heart. Both strengthen the heart's action by stimulation of the muscular tissue of that organ, but they act differently on the frequency of the beat. The chief difference is, however, that caffeine causes dilatation and digitalin contraction of the blood-vessels. In many cases of cardiac degeneration where digitalis is useless caffeine does much good.

The dilatation of the vessels produced by caffeine renders it a valuable drug in cases of cerebral anæmia and consequent headache due to contraction of the cerebral vessels; though whether this drug would be useful in migraine it is impossible at present to say.

W. D. H.

Physiological Action of Cocaine. By C. SIGHICELLI (*Chem. Centr.*, 1887, 1150; *from Arch. Ital. Biol.*, **7**, 128—133).—Cocaine causes complete paralysis of the muscles of the eyeball, and indeed of all small striped muscles. On dropping about 1 c.c. of a 2 per cent. solution of the hydrochloride into the eye, the above takes place in about 10 minutes. It causes widening of the pupil and paralysis of the iris. It has the same action on the smooth muscles of the intestine. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Reducing and Oxidising Properties of Bacteria. By W. HERAEUS (*Bied. Centr.*, 1887, 783—784).—The author prepared pure cultivations of the various bacteria (Bacilli and Micrococci) which occur in river water, in spring water and in soil, and also of the mould fungi (*Mucor* and *Aspergillus flavus*). Besides ash constituents, the nutrient liquids contained either ammonium carbonate or calcium nitrate or carbamide. There were found (besides those bacteria that would not grow in artificial liquids) two species which reduced nitric acid to nitrous acid and ammonia, and converted carbamide into ammonium carbonate; one species which made use of nitric acid without reducing it to nitrous acid and which changed carbamide into ammonium salts; one species which behaved similarly with nitric acid, but which did not change carbamide into ammonium compounds; one species which gave no indications of action on nitrogenous substances; one species which left nitric acid unaltered but changed carbamide into ammonium salts; and lastly two mould fungi which gave no indications of action on nitrogenous substances. No species of bacteria were found which had an oxidising action; but some micro-organisms were obtained from soil infusion and from putrefying urine which converted the nitrogenous matter of both ammoniacal and urine solutions, and of diluted meat-infusion into nitrous acid.

Further an examination for oxidising properties was made with various known species of bacteria; namely, the hay bacillus, *Micrococcus prodigiosus*, Finkler's bacteria; also with the pathogenic ones, namely, those of anthrax and typhus, *Tetragonus* and others. In solutions containing sugar and the ash constituents, almost all of them were devoid of any perceptible growth; whilst in urine diluted with four times its bulk of water, *Micrococcus prodigiosus*, root-shaped bacteria, the spirillum of cheese, Finkler's bacteria, those of typhus and anthrax and *Staphylococcus citreus*, succeeded in forming nitrous acid. Hay bacillus, *Staphylococcus aureus*, and the bacteria of green pus and of pneumonia produced a thick turbidity but no nitrous acid. Brieger's bacteria had a feeble oxidising action, and the experiments with Miller's bacteria gave a negative result. H. H. R.

Spring Sap of the Birch and Hornbeam. By R. HORNBERGER (*Bied. Centr.*, 1887, 821—825).—The sap was drawn from the hornbeam at two spots, the one 0·7 m. the other 4·1 m. above the ground; from the birch at 0·5 m. and 3·5 m. above the ground, and the hours of collection were 10 A.M. and 6 P.M. from April 13 to May 4. The sap of both trees contains lævulose with some dextrose, nitrogen and malic acid and salts; the highest percentage of sugar is found in the sap collected at the upper boring, and the total quantity is also greater, moreover the morning sap is always richer in sugar than the evening, and if the upper opening is closed, then the sugar obtained below is in

greater quantity; there appears also to be a diminution in grams per litre as the season progresses. Comparing the two saps, the hornbeam is poorer in sugar than the birch, the highest yield being 4.72 grams per litre (15.59 in the birch), and this was only obtained at the upper boring and at the commencement of the observation; ever afterwards the quantity decreased: the higher percentage of sugar in the morning sap was found in both trees. Nearly all sugar disappeared before the hornbeam ceased to blossom, whilst it still appeared up to the end of the blossoming of the birch. Malic acid is in larger quantities in both saps at the later periods, and there is no difference by day or night, but it is present in double the quantity in the birch sap, which contains least sugar. The total nitrogen in the birch sap at 3.5 m. height is twice as much as at the lower level, and the hornbeam is much poorer in nitrogen than the other tree; but little of the nitrogen appears as albuminoids, but the albuminoids do increase during blossoming period; the greater portion appearing as amido-acids and in other forms, even as ammonia. The mineral constituents were found to increase during the period of observation; the upper boring yielded a sap richer in minerals than the lower, and the sap is also richest when collected in the evening. With the hornbeam, this is not the case; if any difference is observable it is that the lower sap is the richest. Potash increases in the birch sap as time goes on, the evening sap being richer in it than the morning, the upper than the lower; the same holds good for lime and magnesia. Phosphoric acid increases at the lower boring as the season progresses, but it decreases at the upper; also the evening is richer in this compound than the morning sap, but it is always in larger quantities at this boring. In the hornbeam, this is different, for there is not much variation between the two yields either as time goes on or as the examination is made at evening or morning.

The bases in the birch sap are largely in excess of the mineral acid present, only $\frac{1}{3}$ to $\frac{1}{4}$ being thus combined, and with the hornbeam there is a similar condition of affairs, only that the difference between the amounts of bases and acid is hardly so great. The author considers that the malic acid found in the sap of both trees is present as a bye-product.

E. W. P.

Citric Acid in *Oxycoccus Palustris*. By P. KOSSOVIĆ (*Chem. Centr.*, 1887, 1157, from *J. Russ. Chem. Soc.*, 1887, 272—274).—The amount of citric acid found in three different samples of cranberry, *Oxycoccus palustris*, was 2.0, 2.44, and 2.8 per cent. of the total weight of the berries. As these occur very largely in many districts of the interior and the north of Russia, the author proposes to use their juice for industrial purposes, for instance in dyeing, instead of the concentrated lemon-juice imported from Italy.

J. W. L.

Organic Constituents of the Beetroot Juice. By E. O. v. LIPPMANN (*Ber.*, 20, 3201—3209).—Durin (*Bull. Assoc. Chem.*, 1, No. 5) observed a thick froth, having an odour of butyric acid, to be formed on the surface of the bye-products from the preparation of

sugar when being evaporated down. The author has examined the froth and found that besides the potassium salts of fatty acids, it contains dextran and phytosterin (Hesse, Abstr., 1878, 850).

Beetroot was extracted with a mixture of ether and alcohol, the ether evaporated and the residue dissolved in alcohol and treated with platinum chloride; the precipitate so obtained when purified and decomposed with hydrogen sulphide yielded lecithin. This when boiled with baryta-water yielded oleic acid, glycerol, phosphoric acid, and betaine. The formula of lecithin is probably $C_{44}H_{82}O_9PN$.

A second experiment gave a lecithin which yielded no betaine, but choline.

Betaïne and choline are readily separated by means of the hydrochlorides; betaïne hydrochloride forms stable crystals, whilst choline hydrochloride is very deliquescent.

Beetroot contains also other compounds containing phosphorus which are related to the nucleïns; the products of decomposition of these compounds—the xanthine compounds—are almost all contained in the molasses. (Compare Scheibler, *Annalen*, 148, 77.)

N. H. M.

Chemico-physiological Study of Algæ. By O. LOEW and T. BOKORNY (*J. pr. Chem.* [2], 36, 272—291).—Algæ (*Zygnemacæe*) superficially dried with blotting-paper contain 85—90 per cent. H_2O ; when dried at 100° their composition is—fat 6 to 9 per cent., albumin 28 to 32 per cent., cellulose and starch 60 to 66 per cent. The fat is situated chiefly in the chlorophyll region, but is not visible in drops under ordinary circumstances; lecithin is probably present. The quantity of starch varies very considerably according to circumstances; during copulation its amount decreases and glucose is formed, which otherwise very seldom accumulates in appreciable quantities. The gum is situated in the membrane, the tannin, however, in the substance of the plant. Cholesterin and succinic acid (0.4 per cent.) are also found in algæ, but the xanthines, leucine and asparagine are not present.

For *Zygnemacæe*, nitrates are a more suitable source of nitrogen than ammonia, but this does not apply to all algæ, as some thrive very well in presence of ammoniacal salts. Potassium nitrate is far less suitable than sodium nitrate. *Spirogyræ* when placed in dilute solutions of the former died after four weeks' time, probably from overproduction of starch. Potassium chloride and potassium dihydrogen phosphate do not, however, act injuriously.

Some organic compounds (aspartic acid, succinic acid, hexamethyleneamine, &c.) act nutritiously, especially in the light, but malic and coumalinic acids cause death. Algæ live for weeks in solutions of urethane without injury; in solutions of carbamide they die after a few days, and in a few hours when placed in solutions of guanidine. On the other hand, hydantoin and creatine act beneficially, so that the injurious action of a compound is increased when, by entrance of amido-groups, its alkalinity is increased, but lessened when, by entrance of acid radicles, its alkaline character is diminished.

Ammonia and many organic bases (ethylamine, quinoline, quinine,

&c.) cause granulation in the protoplasm of *Spirogyræ*, and death results, probably owing to polymerisation of the active albumin; their hydrochlorides act similarly, but in a less degree; it is probable, however, that ammonia salts do not act banefully when added in such quantity that the production of albumin and consumption of ammonia keep pace with the supply of the latter. Many other substances (nitrous acid, hydrocyanic acid, potassium chlorate, &c.) cause death more or less quickly, but numerous salts (sodium phosphite, hypophosphite, thiosulphate, barium chloride, potassium ferrocyanide, &c.) have no harmful action.

Algæ kept in the dark lose their starch more rapidly when the temperature is increased; a supply of peptones, however, decreases the rapidity of the absorption. Starch is not produced by *Spirogyræ* when the algæ are placed in a solution containing 0.1 per cent. of sugar; *Vaucheria*, though it produces no starch when placed in a 5 per cent. sugar solution, forms a little when placed in a 20 per cent. solution. *Spirogyræ* deprived of its starch lived in the dark for three weeks in a 0.1 per cent. solution of methylal, but no starch was formed. At the end of this time it was exposed to the light in water containing carbonic anhydride, whereupon starch was produced; a second portion of the same plant died in about three days under similar conditions, but without the addition of methylal. *Vaucheria* placed in 0.2 per cent. methylal solution sent off numerous shoots, whilst in water alone the growth was quite inconsiderable; a 1 per cent. methylal solution can be borne by *Vaucheria* for several days, but in a 0.05 per cent. solution of formaldehyde death soon ensues.

It follows, therefore, that methylal serves as nourishment for algæ, although starch is not formed from it, but it seems that a carbohydrate is first formed which is suitable for the production of cellulose, and the authors conclude that Baeyer's theory of the formation of starch is the correct one, not only from the result of their own experiments, but because it is supported by other facts, especially by the rapid growth of bacteria in solutions containing compounds of methylal.

F. S. K.

Effects of Atmospheric Deposits on Plants and Soil. By E. WOLLNY (*Bied. Centr.*, 1887, 721—723).—The author has experimented on this subject, employing flower pots with closed bottoms and of about 4 litres capacity. These were filled with a soil rich in humus, containing in different pots amounts of water varying from 10 to 100 per cent. of the quantity the soil could hold when fully saturated. The plants experimented on were peas, rye, rape, and a grass mixture. Additions of water were made from time to time to make up for evaporation and preserve a constant degree of moistness. At the end of the experiments the crops were weighed. The following results were obtained:—1. A proper supply of water is by far the most potent factor in producing a good crop. 2. Up to a certain limit, increase of water gives increased yields, but beyond that limit further increase of water produces a continuous diminution in yield, which falls almost to zero when complete saturation of the soil is reached. 3. Within the limit mentioned, different plants are

affected in different degrees by the amount of water. 4. The most favourable amount of water is different at different stages of growth.

The observations that have been made up to date lead to the conclusion that the maximum yield is obtained within a limit lying between 40 and 80 per cent. of the amount of water the soil can hold when fully saturated. In the case of each particular plant, the amount of water giving the best yield is higher, the more fertile the soil, the more the climate favours the development of the organs of transpiration, and the closer together the plants are situated. As regards the duration of growth, the smaller the water supply the shorter this period is, and in a drought the plants are more liable to die before they are perfectly developed, and to become prematurely ripe the closer they are together. The chemical composition of the grain is also affected by the supply of water; analysis shows that dryness of soil favours the development of a compact, glassy grain rich in nitrogen, whilst in moist situations the grain is less compact in texture, more mealy, and proportionally poor in nitrogen.

H. H. R.

Testing Soil by the Growth of Oats. By A. ATTERBERG (*Bied. Centr.*, 1887, 723—728).—At the Calmar experimental station in Sweden, a soil suspected of having a deficiency of nitrogen and magnesia was examined as follows:—Portions of it placed in tin vessels were sown with black bearded oats, which were manured in some cases with nitrogen, in others with magnesia, and in others no manure was applied. Part of the plants were cut when the panicle had emerged from the sheath, and the rest when the oats were fully ripe. The results were determined as regards (1) the oats cut green, (2) the ripe straw, and (3) the ripe grain.

Where magnesia had been applied, the results were negative. From the comparison of the oats manured with nitrogenous manures with the unmanured crop the following inferences are drawn:—(1.) Liberal nitrogenous manuring considerably increased, not only the weight of the crop, but also the amount of nitrogen both in the ripe and unripe plant. (2.) This was accompanied by a material diminution in the amounts of potash and silica. (3.) The amounts of lime and magnesia were less affected. (2) and (3) are attributed to the fact that the soil, which was very poor in nitrogen, was not rich enough in available potash and phosphates to properly meet the demands of the luxurious vegetation induced by the nitrogenous manuring, but was rich enough, however, in lime and magnesia.

This suggested experiments with potash and phosphates in addition to nitrogen as manuring agents, and these experiments showed—1. That manuring with phosphates produced an increase of phosphoric acid throughout the plant, whilst, notwithstanding that the crop had not increased, the amount of nitrogen diminished in the cases of the plants cut green and of the ripe straw. 2. That manuring with potash was accompanied by a material increase of crop, and that here not only was the amount of potash raised, but also the amounts of nitrogen and phosphoric acid were considerably lowered in both the plants cut green, the ripe straw, and the ripe grain.

The author also conducted some sand culture experiments on the same kind of oats by Hellriegel's method, and found equally remarkable relations among the constituents.

In the first set, varying quantities of nitrogenous manures were applied, and the results showed that the smaller the application of nitrogen, the smaller is the amount of it in the plant and the greater is the amount of phosphoric acid, of magnesia, and in most cases of potash and lime.

In the second set, varying quantities of phosphates were applied, and the results showed that the smaller the application of phosphates the smaller is the amount in the plant, and the greater is the amount of nitrogen and of potash. In the grain, the amounts of potash and magnesia are more constant, and the amount of magnesia appears to follow that of the phosphoric acid.

In the third set, varying quantities of potash were applied, and the results showed that the smaller the application of potash, the smaller is the amount of it in the plant, whilst the amounts of nitrogen, phosphoric acid, and magnesia rise regularly. This did not hold in cases where the growth of the plant was checked, for here the composition was that of the unripe plant.

In the fourth set, varying quantities of magnesia were applied, and the results showed that the smaller the application of magnesia, the greater is the amount of nitrogen and phosphoric acid, at least in the unripe plant and in the straw; the amount of lime also increases regularly.

The author sums up thus:—In the case of a plant-food, if the quantity available for the plant diminishes, then diminishing amounts of it are taken up and assimilated, and the quantity in the plant also sinks. This is accompanied by a feebler development of the plant, and consequently by a smaller crop; thus the other foods are in excess relatively to the food present in a minimum degree, and so are taken up and assimilated in increasing quantities. H. H. R.

Influence of Lime as a Soil Constituent on the Development of Plants. By E. W. HILGARD (*Bied. Centr.*, 1887, 738—739).—In general, the effect of a large proportion of lime is to encourage a low, compact growth and increased fruitfulness, whilst a deficiency of lime in a soil, otherwise of good composition, produces a thin growth and diminished fruitfulness. The droughty territories of Arizona, California, and Oregon show this on a large scale in the low and compact forms of their trees, which are less due to the parching sun than to the high proportion of lime, all the greater there for the want of a liberal rainfall to dissolve it away. H. H. R.

Injury to Vegetation by Sulphurous Acid. By L. JUST (*Bied. Centr.*, 1887, 790).—The injury which some mangolds planted near a cellulose factory had suffered, proved on chemical investigation to have been due to the sulphurous acid in the gases from the factory.

The figures obtained show that the amount of sulphuric anhydride in the diseased plants is abnormal, and is higher than in the uninjured ones. H. H. R.

Manuring Hops. By C. KRAUS (*Bied. Centr.*, 1887, 785—786).—In general the manure should contain three plant-foods, phosphoric acid, potash, and nitrogen, and contain some organic substance, which by its decay will slowly render those foods available. Guano made from fæces in moderate dressings is preferable to the potash-ammonia-superphosphate formerly recommended; it acts better even than mixtures of sodium nitrate and superphosphate containing the same amounts of plant-food. Rape-cake meal would appear to be suitable on the above grounds, and in France it has been found to give good results. These manures are like farmyard manure both in chemical nature and physical effects, and, as with farmyard manure, care must be taken to avoid over manuring. Although nitrogen is of the greatest importance to the hop, as it is to other plants, yet it is possible to give too much of it, and so cause injury. If nitrogenous manures are employed alone on the poorer soils, the yield will not be a full one, and even on the better soils the crops will in time fall off. Potash and phosphates should only be employed without nitrogen when a trial has proved that there is enough nitrogen stored up in the soil, and that nitrogenous manuring will not increase the yield without injuring the quality.

In good situations, artificial manure in addition to farmyard manure is the best means of realising the profit which the locality affords.

H. H. R.

Manuring Sugar Beets with Basic Slag. By E. v. PROSKOWITZ (*Bied. Centr.*, 1887, 739—742).—The trial was made in Kwassitz on an alluvial soil in low marshy country. The plots were 100 square metres (0·025 acre) in area. The manures employed were a basic slag and a superphosphate. The slag contained 20·5 per cent. of phosphoric anhydride, only 0·04 per cent. being soluble in citrate solution. Its state of division was one of medium fineness. The superphosphate contained a total of 17·3 per cent. of phosphoric anhydride, 12·44 per cent. being soluble in water.

The unmanured plots all suffered from root decay. The best matured roots (as indicated by their having the smallest proportion of leaves to roots) were on the plots manured with superphosphate. The author concludes that in that particular neighbourhood, on heavy clay land, the basic slag was less effectual than the customary quantity of superphosphate, and that the time of applying it had no decided influence.

H. H. R.

Comparison of the Different Properties and Character of Manure made with Straw and with Turf Litter. By M. FLEISCHER (*Bied. Centr.*, 1887, 808—814).—As regards the value of straw or peat alone as manure, it appears that straw contains most potash, lime, and phosphoric acid, whilst peat moss litter contains most nitrogen, and when mixed with manure the peat manure contains more easily soluble nitrogen than the straw manure; the retention of soluble nitrogen (ammoniacal compounds) by peat therefore renders it somewhat more valuable than straw. Field experiments show that peat makes the better manure, especially on light land,

because of its retentive capacity for soluble nitrogen, consequently the after effects are greater than when straw is employed. On heavy lands, however, the question is not yet decided. E. W. P.

Behaviour of Various Plants towards Nitrogenous Manures.

By E. WOLFF and C. KREUZHAGE (*Bied. Centr.*, 1887, 793—808).—The object in view was not to estimate the capability of plants to absorb nitrogen from the air either directly or indirectly, but rather to collect facts to prove that various plants are differently influenced by nitrogenous manures. To this end plants were sown in artificial soils, the base being sand, in some cases calcined, in others in the ordinary state, and the experiments extended over some years. Some plants received no added nitrogen, whilst others received increasing quantities. Full details of the weight of the crops harvested, the manures, &c., are given. The yield of straw crops (oats, &c.) is greatly increased by the addition of Chili saltpetre, but Leguminosæ, beans, lupines, clover, &c., are not increased in yield even when the amount of added nitrogen is trebled. Beans, &c., remove from the soil more nitrogen than is contained in the original seed and the manure, whilst the opposite is the case with oats, &c. E. W. P.

General and Physical Chemistry.

Degree of Oxidation of Chromium and Manganese in Fluorescent Compounds. By L. DE BOISBAUDRAN (*Compt. rend.*, **105**, 1228—1233).—This paper contains details of the results obtained by calcining, in air or in hydrogen, mixtures of pure alumina with chromic oxide; of gallium oxide and chromic oxide; of calcium oxide and chromic oxide; of magnesium oxide and chromic oxide; of alumina with small quantities of potassium and manganese oxides; and of calcium and manganese oxides.

Too large a proportion of chromium reduces and may even destroy the fluorescence. In some cases, calcination in hydrogen reduces, in others it intensifies the fluorescence, but no general conclusions are drawn as to the influence of the degree of oxidation on the phenomenon. C. H. B.

Rotatory Dispersion. By L. GRIMBERT (*J. Pharm.* [5], **16**, 295—300; 345—350).—The author employed Laurent's polarimeter and monochromatic light. To obtain rays near to λ , a layer 1 cm. thick of the following solution was used:—Carmin No. 40 0.25 gram, ammonia 20 c.c., water to make up to 100 c.c. With white light, this solution gives a spectrum reduced to a very narrow band coinciding with the C line. On taking the rotative power of an active substance in this light and also in the sodium light, two different values are obtained, $[\alpha]_D$ and $[\alpha]_C$. The ratio $[\alpha]_D/[\alpha]_C$ gives the dispersive power. Usually tubes of 200 mm. length were employed; sometimes 100 mm. tubes were used, as, for example, when the deviation was over 20° .

Saccharose.—Both water and alcohol were employed as solvents. The rotative power varies neither with the concentration nor with the solvent: $[\alpha]_D = +66.45^\circ$; $[\alpha]_C = 52.85^\circ$; and $[\alpha]_D/[\alpha]_C = 1.257$.

Lactose.—It is well known that the rotative power of lactose diminishes rapidly when first dissolved in the cold. The rotative power does not vary with the concentration. It is $[\alpha]_D = +52.37$ and $[\alpha]_C = +41.58^\circ$. The ratio between the rotative power when first dissolved to that when it becomes stationary is as 8 : 5. The dispersive power is $[\alpha]_D/[\alpha]_C = 1.259$, and is constant during the time the rotative power is passing to the minimum. It does not vary with the concentration of the solution.

Maltose.—When dissolved in the cold, the rotative power of maltose increases to a maximum. Its dispersive power is 1.262, and is constant during the time the rotative power is changing.

Glucose acts like lactose. The ratio between the initial and final rotative powers is as 2 : 1. The dispersive power is 1.258, and is constant whilst the rotative power is passing to the minimum.

Morphine Hydrochloride.—Solutions of different degrees of concentration confirmed the value given by Hesse, $[\alpha]_D = -100.67^\circ - 1.14 C$.

The dispersive power $[\alpha]_D/[\alpha]_C = 1.284$, and does not vary with the concentration.

Codeine.—In absolute alcohol, $[\alpha]_D = -134.24^\circ$, and in chloroform -114.82° , but the dispersive power only varies slightly and is on the average 1.268.

Brucine.—Anhydrous brucine, dissolved in absolute alcohol and in chloroform, gave values for $[\alpha]_D$ confirming those obtained by Oudemans. The dispersive power does not vary with the nature of the solvent, and is $= 1.357$, the highest hitherto observed.

Quinine.—The hydrate, dissolved in absolute alcohol, and in chloroform; the basic hydrochloride dissolved in water; and the normal sulphate dissolved in water, and in 90° alcohol, all give the same dispersive power of 1.313, the variation in the solvent and in the acid combined with the base producing no change in this respect.

Cinchonine.—The basic sulphate was observed when dissolved in water, absolute alcohol, and chloroform. Although the nature of the solvent has considerable effect on the rotative power of the salt, the dispersive power remains constant and equal to 1.268.

Strychnine.—Two samples of different character were recrystallised from alcohol, and dissolved both in 80° alcohol and in chloroform. Notwithstanding considerable differences in the rotative power of the two samples in both solvents, the dispersive power was constant and equal to 1.313.

Camphor.—This substance was recrystallised from alcohol and fused. It was dissolved in alcohol of various strengths, in chloroform, and in dry ether. The rotative power varies with the nature of the solvent; its dispersive power is sensibly constant. In alcoholic solution, the rotative power increases with concentration of the alcohol. In dry ether, the rotative power does not vary with the concentration of the solution. In chloroform, as well as in alcohol, the dispersive power remains constant, notwithstanding that the rotative power increases with the concentration.

Cholesterin.—This was observed in ether and chloroform. Its dispersive power averages 1.323. It does not vary, like the rotative power, with the nature of the solvent.

Essence of Térébenthine.—A lævorotatory sample gave—

$$[\alpha]_D = -30.46, [\alpha]_C = -28.57, \text{ and } [\alpha]_D/[\alpha]_C = 1.241.$$

The results obtained with the foregoing substances show that the dispersive power remains constant whatever be the concentration of the solution; that the dispersive power of those substances whose rotative power varies with the temperature, remains constant all through that variation; that for the same substance it scarcely varies with the nature of the solvent; that each substance has its own proper dispersive power which seems to bear no relation to the chemical constitution of the substance, although it may be noted that the sugars have all the same value.

J. T.

Distribution of Electromotive Force in the Cells of Batteries.
By J. MIESLER (*Monatsh.*, 8, 626—631).—The author has extended the work of Moser (this vol., p. 209) to the batteries of Grove,

Bunsen, Grenet, Smee, Lalande, and Leclanché. In every case, the total electromotive force of the battery under examination was found to be equal to the sum of the electromotive forces between the different parts of the cell. G. T. M.

Electrochemical Studies. By W. OSTWALD (*Zeit. physikal. Chem.*, **1**, 74—86 and 97—109).—From his former experiments (*J. pr. Chem.*, 1884—1886), the author has drawn the conclusion that the molecular conductivity increases for monobasic acids with increasing dilution, tending to a maximum value which it was thought would prove to be the same for all acids. On careful repetition of these experiments, the latter view is found to be incorrect, as the maxima observed for a dilution of 1024 litres differ for 15 different acids by as much as 12 per cent. That this difference does not affect the proportionality between the maximum conductivity and the rate of chemical action of these acids is proved by experiment, the latter being in fact proportional to the relative observed maximum conductivity. A difficulty, however, obviously arises in determining the value of this maximum for feeble acids of low conductivity.

To overcome this, Kohlrausch's law that the conductivity of a neutral salt may be represented as a sum of two constants, one of which depends on the nature of the acid and the other on that of the base, is resorted to. It is shown by the determination of the conductivities of a number of sodium salts of acids of known conductivity that a constant difference exists between the two. The same holds good for lithium and potassium salts, which also differ in conductivity from the sodium salts by a constant fixed quantity. The molecular conductivities of different salts having the same base, differ very largely amongst themselves, and altogether contradict the opinion of Arrhenius and Bouty that the molecular conductivities of dilute salt solutions are the same. The numbers prove, however, that it is possible to represent the conductivity of an acid by that of one of its salts, plus some constant. The determination of these constants is reserved for a future paper.

Another interesting result is that there is an almost constant increase in the molecular conductivity of the sodium salts of the monobasic acids, with an increase in the dilution of from 32 to 1024 litres, varying between 10 and 13 units. The poorer conductors give the smaller value, so that the increase appears to depend partly on the conductivity. For bibasic acids it has about double the above value, and is nearly three times as great for tribasic. Polyvalent bases act similarly to polyvalent acids although not quite so regularly. It would seem, in fact, that if m is the molecular conductivity, and v the dilution, dm/dv is of the form $n_1 \times n_2 \times \text{const.}$, where n_1 is the valency of the acid, and n_2 that of the base. According to this mode of testing, dithionic acid appears to be truly bibasic. H. C.

Pyrometer. By J. MENSCHING and V. MEYER (*Zeit. physikal. Chem.*, **1**, 145—158).—The advantage of the instrument presently to be described is that it affords a quick as well as an exact measurement of temperature. The principle of the method is to determine

the temperature from the measurement of the volumes of gas contained in the instrument at the temperature of the laboratory and at the higher temperature that is required. Part of the instrument is at a low temperature, but error from this cause is obviated by means of a compensator.

The instrument consists of a vapour-density vessel, a platinum cylinder 200 mm. high and 36 mm. in diameter. To the middle of one end of the cylinder is connected a platinum tube 350 mm. long and 4 mm. in diameter. Close by the side of this tube runs a platinum capillary tube with very thick walls, which passes through the circular end of the vapour-density vessel and goes down to within 3 mm. of the bottom. The end of the capillary tube is bent round through a right angle. The compensator is composed of a platinum tube connected at one extremity with a capillary tube, so that it is of exactly the same shape and size as the part of the instrument outside the cylinder. The instrument was heated by Perrot's gas-oven, by means of which a temperature of about 1500° can be produced.

Incandescent platinum, as Deville and Troost have shown, is permeable by hydrogen but not by air. The platinum cylinder was therefore surrounded by a Berlin porcelain tube which is impermeable to all gases.

In making an experiment, the platinum cylinder was filled with nitrogen by an india-rubber tube attached to the capillary tube, and communicating with a series of drying tubes connected with a gasometer. The quantities of gas contained in the whole instrument and the compensator at the higher temperature T were measured, and the difference reduced to volume at temperature 0° and normal pressure. Then V being a similar quantity for the temperature of the laboratory, T is given by—

$$T = (V - v) / (V\alpha - V\gamma),$$

when α , γ are the coefficients of cubical expansion of platinum and nitrogen.

C. S.

Specific Heat of Tellurium. By C. FABRE (*Compt. rend.*, **105**, 1249—1251).—Tellurium was precipitated by means of sulphurous acid, washed with water saturated with nitrogen, and dried in a current of nitrogen. The mean of three determinations of the specific heat is 0.05252. The same tellurium was volatilised in a current of sulphurous anhydride, and was thus obtained as a black sublimate with a crystalline fracture, different in appearance from the product obtained by distillation in hydrogen. Determinations of the specific heat gave 0.05182.

Crystallised tellurium was prepared by the decomposition of alkaline tellurides, washed with water saturated with nitrogen, distilled in a current of hydrogen, fused, and allowed to cool slowly. It had a crystalline fracture. Two determinations of the specific heat gave as the mean 0.048315.

From these results, it follows that the various forms of tellurium have sensibly the same specific heats at temperatures near 100°

Possibly differences may appear at higher temperatures, and especially near the point of transformation of amorphous tellurium into the crystalline variety.

C. H. B.

Constancy in the Heat produced by the Reaction of certain Salts on each other. By S. U. PICKERING (*Chem. News*, 57, 75—77).—The author shows that the constancy in the heat evolved in the reaction of silver nitrate on metallic chlorides in solution, observed by Richards (*Chem. News*, 57, 16), is an inevitable consequence of the heat of neutralisation of hydrochloric and nitric acids being independent of the nature of the alkali, the number 16165 cal. being merely the heat of precipitation of silver chloride. Similarly, the heat measured by Fay on adding barium chloride to sulphates is the heat of precipitation of barium sulphate, 5580 cal. In this case, however, it is constant only when dyad metals are concerned, since it is only with these that the difference between the heat of neutralisation of the hydrate with sulphuric and hydrochloric acids is a constant quantity. The quantities determined by Fay have already been determined by Thomsen. S. U. P.

Heat Equivalents of Benzoyl Compounds. By F. STOHMANN, P. RODATZ, and W. HERZBERG (*J. pr. Chem.* [2], **36**, 353—370).—The authors, continuing their previous work (Abstr., 1887, 878), have determined the heat of combustion (in free oxygen) of the following benzoyl-compounds:—

	Heat equiv. per gram-mol.	Heat of formation.
Glyceryl benzoate, C ₃ H ₅ (C ₇ H ₅ O ₂) ₃	2720536	225464
Mannityl benzoate, C ₆ H ₈ (C ₇ H ₅ O ₂) ₆	5361915	461085
Benzophenone, COPh ₂	1557556	9444
Acetophenone, COMePh (solid)	1001400	26600
" " (liquid)	1003440	24560
Methyl salicylate, OH·C ₆ H ₄ ·COOMe	898776	129224
Ethyl " OH·C ₆ H ₄ ·COOEt	1051748	139252
Propyl " OH·C ₆ H ₄ ·COOPr	1206120	147880
Isobutyl " OH·C ₆ H ₄ ·COOBu ^β	1366270	150730
Methyl parahydroxybenzoate, OH·C ₆ H ₄ ·COOMe (solid)	889200	138900
Ethyl parahydroxybenzoate, OH·C ₆ H ₄ ·COOEt (solid)	1043310	147690
Propyl " OH·C ₆ H ₄ ·COOPr (solid)	1201117	—

Comparing the differences of the heat equivalents of the benzoates, salicylates, and parahydroxybenzoates, the authors calculate the heat of combustion for salicylic acid to be 723600 cal., that of parahydroxybenzoic acid 715839 cal. Thus, whilst the substitution of a hydrogen in benzoic acid to form salicylic acid decreases the heat-value 46833 cal., a similar substitution to form the para-acid decreases it 54628. The latter number is very close to that found in the formation of phenols from benzene, and it therefore appears that the

para-acid more closely corresponds with the phenols than the ortho-acid does.

Glyceryl benzoate was prepared by the action of glycerol and soda on benzoic chloride. It forms long, silky needles melting at 72.4° . *Mannityl benzoate* forms colourless scales melting at $124-125^{\circ}$.

L. T. T.

Boiling Points and Specific Volumes of the Normal Fatty Ethers. By P. DOBRINER (*Annalen*, 243, 1-22).—The author's experiments lead him to the following results. In the case of metameric ethers, the boiling point falls as the difference in the number of carbon-atoms in the two alcohol radicles diminishes. Methyl ethers have the highest boiling points. In a series of homologous ethers containing one alcohol radicle in common, the difference between the boiling points diminishes as the carbon-atoms increase in number. Methyl ethers form an exception to this rule, as the difference between the boiling points of the methyl and ethyl ethers in such an homologous series is smaller than the difference between the ethyl and propyl ethers.

The boiling points of amyl and hexyl ethers can be calculated approximately, as the difference between the boiling points of homologous amyl and hexyl ethers is equal to one-third of the difference between butyl and heptyl ethers. The difference between butyl and amyl ethers is a little larger, and the difference between hexyl and heptyl ethers is a little less.

The difference between the boiling points of methyl and ethyl compounds is smaller than the difference between ethyl and propyl compounds when the alcohol radicles are directly attached to an oxygen-atom (for instance, in the case of the methyl, ethyl, and propyl salts of the adipic acids), but the case is reversed if the alcohol radicles are directly united to carbon-atoms.

Specific Gravity.—In the case of metameric ethers, the highest specific gravity is exhibited by the ether with the highest boiling point, and the lowest specific gravity by that of the lowest boiling point. In an homologous series, the specific gravity at 0° increases with the carbon-atom, but the specific gravity at the boiling point diminishes as the compounds increase in carbon.

Specific Volume.—The specific volume of an ether is approximately identical with that of an ethereal salt, the radicles of which contain the same number of carbon atoms. The specific volumes of the ethers are larger than the specific volumes of the metameric alcohols. In a series of metameric ethers, the methyl ether has the smallest coefficient of expansion.

W. C. W.

Specific Volumes of Normal Alcoholic Iodides. By P. DOBRINER (*Annalen*, 243, 23-31).—The specific volumes of the following iodides were determined:—

CH_3I ,	64.1	$\text{C}_5\text{H}_{11}\text{I}$,	151.2
$\text{C}_2\text{H}_5\text{I}$,	85.7	$\text{C}_6\text{H}_{13}\text{I}$,	175.5
$\text{C}_3\text{H}_7\text{I}$,	106.8	$\text{C}_7\text{H}_{15}\text{I}$,	198.6
$\text{C}_4\text{H}_9\text{I}$,	128.5		

The specific volume of an iodide $C_nH_{2n+1}I$ is the same as that of an acid of the formula $C_nH_{2n+1}COOH$. W. C. W.

Boiling Points and Specific Volumes of Phenols and their Ethers. By J. PINETTE (*Annalen*, **243**, 32—63).—In homologous ethers of the same phenol, the difference in the boiling points of the methyl and ethyl ethers is about 5° less than the difference between those of the ethyl and propyl ethers. In ascending the series from the ethyl ethers, the difference gradually diminishes. The difference between phenol and thymol ethers of the same alcohol radicle decreases with an increase of carbon in the alcohol radicle. Meta- and para-cresol have almost the same boiling point, this is also true of their metameric ethers. Orthocresol boils about 11° , and its ethers about 6° lower than the corresponding meta- and para-compounds. The boiling points of propyl, butyl, and octyl phenyl ethers are almost identical with the boiling points of the metameric ethers of meta- and para-cresol, and are higher than the orthocresol and thymol-derivatives.

The difference between the boiling point of a phenol and its methylic ether decreases with the increasing molecular weight of the phenol.

Specific Volume.—Phenols have a smaller specific volume than the metameric ethers. The specific volumes of phenol and its ethers coincide with those of butyl alcohol and its ethers. Meta- and para-cresols and their ethers have approximately the same specific volumes; they are about 1 per cent. higher than the corresponding orthocresol-derivatives. The specific volumes of the thymol ethers are relatively small.

The author obtains the following values for the specific volumes of the isomeric xylenes:—

	Ortho.	Meta.	Para.
	137·6	139·75	139·9
Schiff found	139·9	139·7	140·2

W. C. W.

Boiling Points and Specific Volumes. By W. LOSSEN (*Annalen*, **243**, 64—103).—The author has compared the boiling points of a large number of organic compounds, and agrees with Dobriner (preceding page) that in an homologous series, the first difference (that is the difference between the boiling points of methyl and ethyl compounds) is less than the second (namely, between ethyl and propyl) when the alcohol radicle is attached to the rest of the molecule by an oxygen-atom. When the radicle is attached to a carbon-atom, the reverse is true in the majority of cases. In many cases, the first and second differences are equal, and in a few cases the first difference is a little less than the second.

The author agrees with Horstmann (*Abstr.*, 1886, 759) that a comparison of molecular volumes determined at the same temperature possesses many advantages not shared by specific volume determinations at the boiling point. W. C. W.

Estimation of Vapour-densities. By C. SCHALL (*Ber.*, **21**, 100—101).—Further modifications in the apparatus lately described by the author (*Abstr.*, 1887, 695, 882). J. W. L.

Determination of Vapour-density at Low Pressure. By H. MALFATTI and P. SCHOOP (*Zeit. physikal. Chem.*, **1**, 159—164).—In spite of the many modifications of methods of measuring vapour-density, there is not at present a convenient method when the tension is small. Hofmann's method requires for small tensions a cumbrous apparatus, whilst in Habermann-Dumas' method there is the objection of the additional determination of the weight of the vapour.

A tubular glass vessel of 100 c.c. capacity closed at one end is carefully cleaned and dried. Inside the tube is placed a short barometer tube. The substance is weighed in a small glass sphere having two sides drawn out into fine tubes; one capillary tube is stopped with alloy, and the other hermetically sealed after the introduction of the substance. The end of the glass vessel is drawn out into a capillary tube and the air is exhausted from the vessel; when the levels of the arms of the barometer tube remain unaltered the vessel is hermetically sealed. It is next immersed in a bath of known temperature, and the difference of level of the arms of the barometer is read off by a millimetre scale, so that the pressure is known. The vessel is immersed in water and the capillary point broken off. The vessel when filled is weighed. Thus, having measured the volume of a given length of the barometer tube, we have sufficient data to determine the vapour-density.

In order that the barometer may contain no moisture, it is constructed as follows:—A tube is bent into the form of a double U-tube, and one end is passed through a cork inserted in the neck of a fractional distillation flask which contains a small quantity of mercury. The flask is inclined, so that the end does not touch the mercury, and heated while dry air is drawn through the tube. When the flask is placed upright, the tube is immediately filled with mercury.

The proper quantity of substance to be placed in the sphere is determined by a preliminary calculation. For higher temperatures, the barometer is filled with an alloy of 3 parts lead and 1 part tin, which does not stick to the tube and has no perceptible tension.

For higher temperatures, the author also shows that a modification of L. Meyer's apparatus (*Ann. Phys. Chem.* [2], 1880, 550) can be employed. C. S.

Viscosity of Dilute Aqueous Solutions. By S. ARRHENIUS (*Zeit. physikal. Chem.*, **1**, 285—298).—The solution is contained in a glass sphere of volume 0.9846 c.c., and is allowed to flow vertically through a fine capillary tube, the bore of which suddenly enlarges at its lower end, so that the velocity of efflux is negligible. The flow of liquid may be started by turning on a tap connected with the upper part of the sphere. The sphere and the capillary tube connected to it are immersed in a water-bath so that the solution may be kept at a known temperature. Since the liquid escapes with a very small velocity, the work done by the solution in falling through the height of the capillary tube will be entirely spent in overcoming the resistance due to viscosity, provided no energy is consumed in setting up vortex-motion as the liquid passes from the capillary tube into its enlarged end. In any case, the energy so spent will be less than if all the kinetic energy

of the liquid passing into the enlargement were employed in setting up vortex-motion. But on this hypothesis the energy spent may be calculated by a formula given by Hagenbach (*Ann. Phys. Chem.*, 109, 385), and was found to be negligible with the dimensions of the apparatus used by the author. Thus a correction, which has been calculated by various experimenters on hypotheses never completely satisfied, is entirely avoided. By placing the capillary tube vertical, the small particles which are seen to form are carried away and not left adhering to the sides of the tube. Hence the coefficient of relative viscosity, η , will be given by $\eta = (st)/(ST)$, when s is the specific gravity of the solution, t the time of efflux of the volume contained in the sphere, and S, T similar quantities for water.

The results of numerous experiments show that the relative viscosity of a dilute aqueous solution of two different substances is equal to $A^x B^y$, where x, y are the volume percentages of the two substances, and A and B two functions of the temperature which remain constant for the same temperature and the same substance. There does not appear to be any connection between A and the viscosity of the corresponding substance. The constant A diminishes as the temperature increases in the case of non-conductors, so that the values of the relative viscosity tend to a common limit, unity. The viscosity of water is increased by the addition of a small quantity of a non-conductor. Those normal solutions which have greater conductivity have in general less relative viscosity, but there does not seem to be any simple law connecting conductivity and viscosity. C. S.

Dissociation of Hydrated Salts. By P. C. F. FROWEIN (*Zeit. physikal. Chem.*, 1, 5—14 and 362—364).—The relation which must exist between the heat of combination of the water in hydrated salts and the maximum vapour-tension has been thermodynamically calculated, but hitherto has not been experimentally established in a satisfactory manner. This is the aim, therefore, the author has in view.

The thermodynamical relation given by Van't Hoff, $d \cdot lK/dT = q/2T^2$, is transformed, in order to be applicable to calorimetric work, into $d \cdot lF/dT = Q/2T^2$, where T is the absolute temperature, Q the amount of heat evolved by the absorption of 18 kilos. OH_2 by the dehydrated salt, and F the ratio of the maximum tensions of salt and water. By integration of the above on the assumption that Q remains constant between small limits of temperature—

$$Q = \frac{2T_1 T_2}{T_1 - T_2} l \frac{F_1}{F_2}.$$

This equation does not, however, give numbers agreeing with Thomsen's observed values for the heat of combination in the cases of $\text{CuSO}_4 + 5\text{OH}_2$; $\text{BaCl}_2 + 2\text{OH}_2$; $\text{SrCl}_2 + 6\text{OH}_2$; $\text{MgSO}_4 + 7\text{OH}_2$, and $\text{ZnSO}_4 + 7\text{OH}_2$, if the values for $F_1 F_2$ are calculated from the numbers given by Pareau and Wiedemann for the vapour-tensions.

Attributing this to errors in the vapour-tension determinations, arising partly from the very small differences in pressure which have to be observed, the author has redetermined these by means of an

apparatus in which olive oil is used in the manometer in place of mercury. The numbers thus obtained for F_1F_2 give values of Q which agree well with those observed by Thomsen for all the before-mentioned salts, with the exception of $SrCl_2 + 6OH_2$. The tension of $Na_2HPO_4 + 12OH_2$ has also been redetermined, and the calculated value for Q brought into agreement with the observed, a result which the former determinations by Debray and Müller-Erbach had not rendered possible.

H. C.

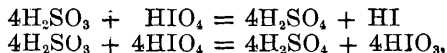
Nature of Chemical Affinity. By W. OSTWALD (*Zeit. physikal. Chem.*, **1**, 61—62).—In a former paper (Abstr., 1886, 294), the author has pointed out that chemical affinity depends not only on the nature and the relative distance of the atoms from one another, but also on the direction in which it acts. The difference in the molecular conductivities of the two nitrosalicylic acids, $[COOH : OH : NO_2 = 1 : 2 : 3$ and $1 : 2 : 5]$, is here offered as proof that although in each the relative positions of the NO_2 and OH to the $COOH$ -group is the same, yet the former acid is the stronger of the two, the closer grouping of the radicles being more favourable to their combined action.

H. C.

Thermodynamical Expression of the Influence of Temperature on the Rate of Chemical Change. By F. URECH (*Ber.*, **21**, 56).—A continuation of the author's investigations (Abstr., 1887, 768). Instead of Van't Hoff's expression, $\log c = -A/T + BT + C$ the equation $\log c = -A'/T + B'$, corresponding with the thermodynamical formula $\log c = -q/RT + B'$, has been applied, and is found to give results agreeing generally with the author's observed values for the rates of inversion of saccharose with hydrochloric acid of different strengths.

H. C.

Action of Sulphurous Acid on Periodic Acid and Rate of the Change. By F. SELMONS (*Ber.*, **21**, 230—241).—The action of sulphurous acid on periodic acid takes place for all proportions of the two acids, the products varying, however, with the amounts employed. A separation of iodine takes place only within the limits represented by the equations—



namely, when more than one and less than 4 mols. HIO_4 enter into reaction with 4 mols. H_2SO_3 , the production of iodine being in fact due to the action of the hydriodic on the iodic acid.

With dilute solutions, the rate of change of the reactions involving the production of iodine from sulphurous and periodic acids can be measured, using starch solution as an indicator. This reaction is similar to that studied by Landolt (Abstr., 1886, 658) on the action of sulphurous acid on iodic acid, and depends on the concentration of the solutions when the proportion between the two acids is kept constant, on the molecular weights for unit concentration, and on the temperature. If C_s is the concentration of the sulphurous, C_p that of

the periodic acid, then the time $t = k_1/(C_s C_p)^z$, where calculated from two consecutive observations, $z = \frac{\log t - \log t_1}{\log (C_s C_p)_1 - \log (C_s C_p)}$. If the sulphurous acid be kept constant in amount, and the periodic acid allowed to vary, $t = k/C_p^y$, where k is constant and y calculated from two consecutive observation $\frac{\log t' - \log t''}{\log C_p' - \log C_p}$. H. C.

Influence of Molecular Contiguity on the Chemical Equilibrium of Homogeneous Gaseous Systems. By SARRAU and VIEILLE (*Compt. rend.*, 105, 1222—1224).—The combustion of organic compounds which do not contain sufficient oxygen for complete oxidation results in the production of a condition of equilibrium between the gaseous products, some of which are completely oxidised, as carbonic anhydride and water, whilst in others, such as carbonic oxide, hydrogen, and methane, oxidation is incomplete. Experiment shows that the conditions of final equilibrium change with an increase in the weight of substance exploded in the same space, that is to say, with an increase in the pressure produced by the products. Two principal reactions are concerned in the progressive alteration of equilibrium. The first $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$, usually occurs; the second, $2\text{CO} + 2\text{H}_2\text{O} = \text{CO}_2 + \text{CH}_4$, takes place when the first has reduced the proportion of water vapour and increased the proportion of free hydrogen to a certain extent, or when the explosive contains so little oxygen that water is formed in relatively very small quantity. The first reaction was observed to take place by Noble and Abel in their experiments with gunpowder. The authors find that it also takes place in the explosion of cotton powder and of picrates. The results obtained with cotton powder, $\text{C}_{24}\text{H}_{29}\text{N}_{11}\text{O}_{42}$, are as follows:—

Density of gas.		Methane.
0.010	$33\text{CO} + 15\text{CO}_2 + 8\text{H}_2 + 11\text{N}_2 + 21\text{H}_2\text{O}$	0.00
0.023	$30\text{CO} + 18\text{CO}_2 + 11\text{H}_2 + 11\text{N}_2 + 18\text{H}_2\text{O}$	0.00
0.200	$27\text{CO} + 21\text{CO}_2 + 14\text{H}_2 + 11\text{N}_2 + 15\text{H}_2\text{O}$	0.006
0.300	$26\text{CO} + 22\text{CO}_2 + 15\text{H}_2 + 11\text{N}_2 + 14\text{H}_2\text{O}$	0.016

The temperature of final equilibrium is about 3000° , the pressure varying between 100 and 4000 atmospheres. The formation of methane, which occurs only to a very limited extent in the case of cotton powder, becomes more marked with such compounds as the lower nitrated derivatives, picrates, and picric acid. The results with the last compound were as follows:—

Density of gas.	
0.10	$11\text{CO}_2 + 84\text{CO} + 24\text{N}_2 + \text{CH}_4 + 16\text{H}_2 + 6\text{H}_2\text{O}$
0.30	$20\text{CO}_2 + 69\text{CO} + 24\text{N}_2 + 7\text{CH}_4 + 7\text{H}_2 + 3\text{H}_2\text{O}$
0.50	$25\text{CO}_2 + 61\text{CO} + 24\text{N}_2 + 9\frac{1}{2}\text{CH}_4 + 4\text{H}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{C}$

The pressures varied from 1000 to 7500 atmos. The reactions which tend to reduce the proportion of carbonic oxide are exothermic

In the case of the first reaction, the development of heat is not great, and there is no alteration in the volume of the gas; but in the second case there is a considerable development of heat, and the volume of the gases taking part in the change is reduced to one-half. The alterations in the conditions of equilibrium tend towards the development of the maximum quantity of heat, and the two reactions concur in making the pressure increase in a greater ratio than the weight of the explosive charge.

C. H. B.

Influence of Neutral Salts on the Rate of Hydrolysis of Ethyl Acetate. By S. ARRHENIUS (*Zeit. physikal. Chem.*, **1**, 110—133).—

In Warder and Reicher's equation for the rate of saponification,

$$-\frac{dC}{dt} = kCC_1, \text{ where } t \text{ is the time, } C \text{ the concentration of the base,}$$

and C_1 that of the salt, k is a quantity which the author proposes to call the specific rate of saponification. This quantity is independent of the amounts of base and salt which act on one another, but most probably varies for different concentrations. In the present case, the influence of the presence of neutral salts on k was studied. This influence is as a rule small, and k remains nearly constant; salts of the halogens and nitrates lower, whilst sulphates and hyposulphites raise the value of k . The influence of potassium iodide is greater than that of potassium bromide, which is greater than that of potassium chloride, the three being very nearly in the ratio 3 : 2 : 1.

Quite abnormal is the influence of ammonia and ammonium salts, the action being very great and varying very distinctly with the amount of salt in solution. k in fact here depends on the amount of dissolved salt, S , according to the equation $k = \frac{A}{1 + aS + bS^2}$

The rate of hydrolysis is practically in all cases proportional to the conductivity. The low conductivity of a weak base such as ammonia, on which other dissolved electrolytes can exercise such a large relative influence, probably explains its abnormal behaviour.

H. C.

Formation and Decomposition of Ethereal Salts: Decomposition of Liquid Tertiary Amyl Acetate. By D. KONOWALOFF (*Zeit. physikal. Chem.*, **1**, 63—67).—Menschutkin (*Abstr.*, 1883, 178, 309) has observed that the rate of decomposition of liquid tertiary amyl acetate at 180° increases until about 50 per cent. of the acetate employed is decomposed, then diminishes, and finally ceases when the decomposition has reached 97.42 per cent. The author shows that the cause of this is the action of the liberated acetic acid on the acetate, and finds that the addition of acetic acid brings about the decomposition of the acetate. By heating amyl acetate with varying amounts of acetic acid for one hour at 159°, he shows that the amount decomposed is dependent on the amount of acetic acid added. This is expressed by the equation $dx/dt = k(100 - x)(x + 2\frac{1}{2}p)$, where x is the percentage of acetate decomposed in the time t , p the quantity of acetic acid added, $2\frac{1}{2}$ the ratio of the molecular weights of the acetate and acetic acid, and k a constant. All other acids have an

action similar to this of acetic acid although in different degree, propionic and butyric acids being far less active.

The action of the haloïd hydrogen acids was also studied, but in these cases the gaseous acid was passed into the liquid acetate at the ordinary temperature. The action is violent, a considerable development of heat takes place, and a tertiary amyl haloïd salt and acetic acid are formed. In the action of hydrogen chloride two stages may be distinguished, the acetate being first decomposed into amylene and acetic acid, and the amylene then combining with the hydrogen chloride. This reaction the author proposes to employ to determine the heat-change represented by $C_5H_{11} \cdot C_2H_3O_2 = C_5H_{10} + C_2H_4O_2$. The comparative ease with which the halogen acids act on tertiary amyl acetate explains the formation of amyl chloride instead of acetate when dimethyl ethyl carbinol is treated with acetic chloride.

H. C.

Chemical Decomposition produced by Pressure. By W. SPRING and J. H. VAN'T HOFF (*Zeit. physikal. Chem.*, **1**, 227—230).—The results of numerous experiments show that in many cases substances which exert no action on each other at atmospheric pressure under ordinary circumstances, can be made to combine more or less completely if they are subjected to a pressure sufficient to cause a perceptible condensation. The researches hitherto made relate to compounds, the volume of which is smaller than that of their constituents. It is therefore a question of some interest and importance to examine whether the temperature of conversion can be lowered in the case of copper calcium acetate, for which the volume is greater than that of its constituents.

In the first experiment the acetate finely powdered at a temperature of 16° was submitted to a pressure of 6000 atmospheres. The powder was thus reduced to a crystalline mass resembling marble, but presenting no sign of chemical decomposition. Next a screw press (*Bull. Acc. Belg.*, **49**, 344) was employed; at a temperature of 40° there were very marked results; three-fourths of the mass being liquefied. On removing the pressure, it became solid again, but the sides of the containing vessel were covered with a coating of copper, and it was possible to pick small leaves of copper out of the mass. The dark blue of the acetate had changed for the most part to green interspersed with white points, showing that the mass had been decomposed into acetate of copper and acetate of calcium. The result was entirely due to the change of volume, since the thermal effect of compression was less than a rise of 1° . When the temperature was raised to 50° , the piston sank without resistance through the mass. The first experiment, which had given a negative result, was now repeated in order to discover whether sufficient pressure had been used, or the result had escaped observation. A press worked by a lever was used, and this time it was found that the piston sank 1.25 mm. in an hour, or, roughly, that the whole could be decomposed in about 110 hours. Lastly, potassium sulphate under the same conditions gave no perceptible diminution of volume. Thus, the higher the pressure and temperature, the more quickly is the acetate decomposed. Since the progress of chemical action depends on the time, it

seems that it is not sufficient to say that the molecules of a substance assume the arrangement which corresponds with the given volume directly it is reached, for a substance can be compressed without altering its state, if the pressure does not last too long. C. S.

Crystallisation of Mixtures. By O. LEHMANN (*Zeit. physikal. Chem.*, **1**, 15—26 and 49—60).—The author discusses the different cases in which mixed crystals have been formed, and the possibility of obtaining such from non-isomorphous forms. He repeats the experiments of Herrmann (*Abstr.*, 1886, 972), on the crystallisation of ethyl quinonedihydroparadicarboxylate with ethyl succinosuccinate with similar results. He also investigates the mixed crystals of ethyl dihydroxyquinoneparadicarboxylate with ethyl tetrahydroxybenzeneparadicarboxylate, and of each of these with each of the two foregoing. These substances, although having a somewhat analogous chemical constitution, differ pretty widely in crystalline form. They give, however, well-defined mixed crystals of form and colour intermediate between those of the two substances of which they are formed.

H. C.

Constitution of Solutions. By F. RÜDORFF (*Ber.*, **21**, 4—11).—Numerous experimenters have found that the solution of a double salt diffuses as if it were a solution of a mixture of its component parts; for this and other reasons, it is generally stated that double salts do not exist as such in solution.

On dialysing solutions of the following double salts, $\text{K}_2\text{SO}_4, \text{NiSO}_4 + 6\text{H}_2\text{O}$; $\text{K}_2\text{SO}_4, \text{MnSO}_4 + 6\text{H}_2\text{O}$; $(\text{NH}_4)_2\text{SO}_4, \text{MnSO}_4 + 6\text{H}_2\text{O}$; $\text{K}_2\text{SO}_4, \text{Cr}_2(\text{SO}_4)_3 + 24\text{H}_2\text{O}$; $2\text{KCl}, \text{CuCl}_2 + 2\text{H}_2\text{O}$; $2\text{NH}_4\text{Cl}, \text{CuCl}_2 + 2\text{H}_2\text{O}$; $2\text{KCl}, \text{ZnCl}_2 + \text{H}_2\text{O}$; $\text{KCl}, \text{MgCl}_2 + 6\text{H}_2\text{O}$; $2\text{NaCl}, \text{CdCl}_2 + 3\text{H}_2\text{O}$; $\text{BaCl}_2, \text{CdCl}_2 + 4\text{H}_2\text{O}$, it was found that the ratio of the metals in the dialysate was entirely different from that in the original liquid; the component parts, therefore, do not form a molecular compound, but exist in solution independently of each other. On the other hand, the following double salts, KCN, AgCN ; $2\text{KCN}, \text{Hg}(\text{CN})_2$; $2\text{KCN}, \text{Cd}(\text{CN})_2$; $2\text{KCN}, \text{Ni}(\text{CN})_2$; $6\text{KCN}, \text{Cu}_2(\text{CN})_2$; $2\text{NaCl}, \text{PtCl}_4 + 6\text{H}_2\text{O}$; $3\text{Na}_2\text{C}_2\text{O}_4, \text{Fe}_2(\text{C}_2\text{O}_4)_3 + 6\text{H}_2\text{O}$; $3\text{K}_2\text{C}_2\text{O}_4, \text{Fe}_2(\text{C}_2\text{O}_4)_3 + \text{H}_2\text{O}$; $3\text{K}_2\text{C}_2\text{O}_4, \text{Cr}_2(\text{C}_2\text{O}_4)_3 + 6\text{H}_2\text{O}$; are not decomposed, but must exist in solution and diffuse as such, inasmuch as the ratio of the metals is found to be the same in the dialysate as in the original liquid.

Several simultaneous experiments were made with each salt, and a membrane prepared from the cuticle of the cæcum of an ox was found to be most suitable, a parchment membrane not being sufficiently homogeneous.

F. S. K.

Absorption of Gases by Petroleum. By S. GNIEWOSZ and A. WALFISZ (*Zeit. physikal. Chem.*, **1**, 70—72).—The statement that a layer of petroleum will protect an aqueous solution from the action of the air has led the authors to examine the absorption of oxygen and other gases by Russian petroleum. The following table contains the results:—

	Absorption coefficients for petroleum at		Ratio.	Water at 20°.
	20°.	10°		
H ₂	0·0582	0·0652	1·2	0·0193
N ₂	0·117	0·135	1·15	0·0140
O ₂	0·202	0·229	1·13	0·0284
N ₂ O	2·11	2·49	1·18	0·670
C ₂ H ₄	0·142	0·164	1·15	0·149
CO ₂	1·17	1·31	1·12	0·901
CO	0·123	0·134	1·09	0·0231
CH ₄	0·131	0·144	1·10	0·0350

The ratio is given on account of E. Wiedemann's statement that the changes which the absorption coefficients of different gases undergo with change of temperature is about the same for all gases; the values for water are given for the sake of comparison. It will be seen that the absorption of oxygen is greater for petroleum than for water, so that the protective action above spoken of must be a doubtful one.

H. C.

Lecture Experiments with Nitrogen Chloride. By V. MEYER (*Ber.*, 21, 26—28).—An experiment is described by which the explosion of nitrogen chloride can be shown, without danger, by allowing turpentine to come into contact with a few drops of the chloride swimming on the surface of the electrolysed ammonium chloride solution contained in an inverted flask, the whole apparatus being placed under a thick glass case.

F. S. K.

Analytical Chemistry.

Gas Receiver for Absorption Analyses. By F. A. WILBER (*Amer. Chem. J.*, 9, 418—420).—A peculiar form of eudiometer intended for the analysis of the gases obtained from potable waters.

Use of Asbestos for Assisting the Subsidence of Suspended Matter. By W. FRESSENIUS (*Zeit. anal. Chem.*, 27, 32—33).—In cases where, owing to the presence of very finely divided suspended matter, as in experiments on artificial digestion, it is difficult to get clear filtration, the subsidence of the solid particles may be greatly assisted by vigorously shaking with fibrous asbestos. M. J. S.

Determination of Sulphur, Chlorine, Bromine and Iodine in Organic Compounds. By P. CLASON (*Ber.*, 20, 3065—3066).—This method consists in burning the substances in air charged with nitric acid. The nitric acid is contained in rolls of platinum gauze 5 cm. long and 1 cm. in diameter, filled with very small glass beads; these rolls absorb the acid readily, and it does not run out when the rolls are placed horizontally. The combustion tube is connected at one end to the air supply, then come two nitric acid rolls, a roll without nitric acid, boat containing the substance, two rolls without nitric acid placed a small distance apart, after an interval two more nitric acid rolls, and lastly a roll without acid; the end of the tube is drawn out, bent downwards, and dips into a flask containing water, or, in the

case of chlorine and bromine combustions, a solution of silver nitrate. The combustion is conducted in the usual manner, the empty rolls in the front part of the tube being first heated to redness, and the substance and acid rolls then so heated that a steady stream of nitrous fumes issues from the exit tube.

A. J. G.

Comparative Value of some Proposed Tests for Nitric Acid.

By P. WALDEN (*Chem. Centr.*, 1887, 1180—1181, from *J. Russ. Chem. Soc.*, 1887, 274—295).—Brucine gives a feeble coloration with solutions of potassium nitrate, 1 : 500000, and of potassium nitrite, 1 : 1100000. Diphenylamine is equally delicate. The author does not recommend phenol or toluidine. For nitrous acid, diamidobenzoic acid, metaphenylenediamine, naphthylamine and amidobenzeneorthosulphonic acid are recommended, their delicacy being 1 : 5000000. The colour reaction with naphthol is not characteristic for nitric and nitrous acids nor for chlorine; it is much less delicate than the brucine and diphenylamine tests. Nitric and nitrous acids in presence of other oxidising agents can be detected in the following way:—Concentrated sulphuric acid and the solution in question are added to an alcoholic solution of β -naphthol. The solution is coloured red, yellowish, or cinnamon, and shows fluorescence, which is not caused by the other oxidising agents. The delicacy is one in 300,000. These reagents can only be used as group reagents, the colours being produced by any energetic oxidising agent. If nitric and nitrous acids are both present, the former can be detected by the compounds mentioned with toluidine. The nitrous acid is then destroyed by an excess of carbamide and sulphuric acid, and the nitric acid which has remained unchanged can be detected by means of brucine or diphenylamine. In water analysis, where there are no other oxidising agents present, brucine, diphenylamine, and metaphenylenediamine are to be preferred to zinc iodide and starch-paste. The author finally recommends a solution of diphenylamine in concentrated sulphuric acid as a reagent for chromic acid, which produces quickly a fugitive blue colour even with a dilution of one part potassium dichromate in 700,000.

J. W. L.

Presence of Sodium Phosphate in Glacial Phosphoric Acid.

By A. BETTENDORFF (*Zeit. anal. Chem.*, 27, 24—26).—The phosphoric acid in sticks found in commerce frequently contains sodium phosphate, which communicates hardness to the otherwise soft glassy acid. It can be detected by dissolving the solid in fuming hydrochloric acid, when the sodium remains undissolved as chloride. A quantity of sodium pyrophosphate (ignited to destroy organic matter) dissolved in hydrochloric acid of 1.19 sp. gr., left 98.5 per cent. of its sodium as chloride. One part of sodium chloride requires 1348 parts of this acid at 12° for its solution. This furnishes a direct method of preparing phosphoric acid from sodium phosphate.

M. J. S.

Estimation of Phosphoric Acid in Basic Slag. By G. KENNEDY (*Chem. Zeit.*, 11, 1089—1091).—The author confirms the opinion expressed by Klein (*Abstr.*, 1886, 835), that there is little or no iron phosphide in basic slag. The phosphoric acid in basic slag

may be accurately determined in the following manner: 10 grams of the finely powdered slag (moistened with alcohol to prevent adherence) placed in a 500 c.c. flask, is heated with 40 c.c. of hydrochloric acid, sp. gr. 1.12, and 40 c.c. of water, for at least a half an hour on a water-bath; if much ferrous salt is present, it is well to add a little nitric acid or bromine before heating. An aliquot part of the filtered solution is mixed with ammonium nitrate and molybdate solution, without previous removal of the silica. The solution, after heating at about 80° for 15 minutes, is filtered, and the precipitate washed with water containing 3 per cent. of nitric acid (to remove adhering iron salts), redissolved in 2.5 per cent. ammonia, and then precipitated with magnesia mixture. The presence of silica does not interfere, owing to the ready solubility of ammonium silicomolybdate in the washing water.

D. A. L.

Estimation of Arsenic in Pyrites. By H. FRESENIUS (*Zeit. anal. Chem.*, **27**, 34—35).—To ascertain whether by fusion the whole of the arsenic could be obtained in alkaline solution, about 10 grams of pyrites was intimately mixed with two parts of sodium carbonate and one part of potassium nitrate. The mixture was fused and thoroughly exhausted by boiling with sodium carbonate solution. The filtrate was neutralised with hydrochloric acid, mixed with ferric chloride, and precipitated by calcium carbonate. The precipitate was distilled with ferrous chloride and hydrochloric acid as long as arsenic passed over. The undissolved residue from the fusion was also dissolved in hydrochloric acid and distilled with ferrous chloride. In the latter distillate, about 9 per cent. of the whole quantity of arsenic was found. The method therefore presents no advantages over direct distillation in a current of chlorine, or distillation with ferrous chloride, after dissolving in hydrochloric acid with addition of potassium chlorate.

M. J. S.

Estimation of Oxygen, Carbonic Anhydride and Carbonic Oxide. By J. SINIBALDI (*Bull. Soc. Chim.*, **48**, 244—246).—An apparatus somewhat resembling Elliott's gas analysis apparatus in principle, but not intelligible without the diagram.

C. H. B.

Apparatus for Direct Determination of Carbonic Anhydride. By O. OSTERSETERZER (*Zeit. anal. Chem.*, **27**, 27—30).—A conical flask of 70 c.c. capacity is closed with a caoutchouc stopper bored with two holes. Through one passes a tube bent at a right angle. This is the inlet for washed air. Below the stopper the diameter of this tube is reduced so that when raised it is loose in the hole. Near its lower end it has a glass hook on which is hung the glass bucket containing the carbonate. At the end it is drawn out to a point which is turned upwards. The other hole carries a Welter's safety bulb tube joined to a Geissler's drying tube. Both of these contain sulphuric acid. Into the upper end of the Geissler's tube is ground a small cylinder for holding pumice saturated with copper sulphate, and the potash bulbs for absorbing the carbonic anhydride are directly connected to the

upper end of this. To use the apparatus, the inlet tube is raised, and the bucket containing the substance is hung on its hook. A small excess of highly dilute acid is placed in the flask, and all the connections are made. The tube carrying the bucket is then pushed down into the acid, its wider portion immediately making it fit tight in the stopper. Purified air is gently aspirated through during the decomposition, and finally the flask is shaken and gently warmed.

M. J. S.

Analysis of German Silver. By F. OETTEL (*Zeit. anal. Chem.*, **27**, 15—18).—This alloy consists of copper, nickel, and zinc, but may also contain tin, lead, iron, cobalt, and manganese. The copper can with certainty be separated from zinc by one precipitation by hydrogen sulphide from a sulphuric acid solution, although not from a nitric acid solution. The solution of 0.5 gram of the alloy in nitric acid (which is consequently free from tin), is evaporated with sulphuric acid, which removes lead. It is then diluted to 100 c.c., acidified with 2 c.c. of strong hydrochloric acid, and precipitated by hydrogen sulphide. It is heated to boiling and re-cooled before filtering, and the precipitate is washed with dilute aqueous hydrogen sulphide, adding a little hydrochloric acid at first.

The filtrate is evaporated to remove hydrochloric acid, diluted, neutralised with potash, mixed with a few drops of sodium acetate, and saturated in the cold with hydrogen sulphide; zinc sulphide separates in a pulverulent form, easily filtered and washed. The hydrogen sulphide is removed from the filtrate by boiling, the iron is oxidised by bromine (not by nitric acid), and precipitated by ammonia. The concentrated filtrate is made strongly alkaline with ammonia and electrolysed. Nickel and cobalt are deposited together on the platinum cylinder, whilst the manganese separates as hydrated peroxide. Precipitation of the nickel by an alkali is only to be trusted when performed in platinum vessels. The copper and lead can also be determined electrolytically. By electrolysing a nitric acid solution of the nitrates with four small Daniell cells, the copper from 0.5 gram of the alloy can be completely deposited in three hours, the lead at the same time separating as peroxide which can be weighed. If a sulphuric acid solution is electrolysed, the copper separates as a red mud, which can be filtered off after stopping the current, leaving the other metals for determination as above.

M. J. S.

Separation of Aluminium and Beryllium. By A. ZIMMERMANN (*Zeit. anal. Chem.*, **27**, 61—63).—Of all the processes hitherto proposed that based on the precipitation of beryllia, when its solution in potash is boiled, seems to be the best. A very pure potash (purified by alcohol and heated till free from organic matter) is requisite. The solution of 0.3 gram of substance must not exceed 300 c.c., or alumina will be precipitated with the beryllia. After 15 to 20 minutes' boiling in a platinum basin much hot water is added, and the beryllia is filtered off and washed. It is free from potassium.

When the two earths are present in about equal quantities, but not otherwise, they may be completely separated by neutralising with

sodium carbonate and boiling with thiosulphate until no more sulphurous acid is given off; 15 to 20 hours' boiling is sometimes necessary. The alumina is precipitated together with sulphur.

M. J. S.

Determination of Alumina in Presence of Iron and Phosphoric Acid. By L. BLUM (*Zeit. anal. Chem.*, **27**, 19—24).—In the technical analysis of such a mixture, it is usual to determine iron and phosphoric acid in two portions of the solution, to precipitate a third by ammonia, and estimate the alumina from the difference. The iron is best determined by precipitation as sulphide after adding tartaric acid. Permanganate gives higher results, owing probably to the presence of organic matter.

The author draws attention to the risk of error in the precipitation of alumina by ammonia. An excess of ammonia re-dissolves the precipitate. The common practice is therefore to boil until the odour of ammonia becomes exceedingly faint. When, however, ammonium chloride is present, the detection of ammonia in the steam by the sense of smell is compatible with an acid condition of the liquid caused by dissociation of the ammonium chloride, and in such a case part of the alumina will be re-dissolved. Presence of ammonium chloride, however, diminishes the solubility of alumina in ammonia, and by using only a small excess of ammonia, and boiling for only a short time, then filtering and washing rapidly, and only with hot water, no loss will be incurred.

M. J. S.

Determination of Traces of Bismuth and Antimony in Commercial Copper. By P. JUNGFER (*Zeit. anal. Chem.*, **27**, 63—65).—On adding sodium carbonate to a nitric acid solution of copper containing bismuth, the latter is precipitated first. After vigorous stirring and remaining for an hour or two, the precipitate can be filtered off, dissolved in a little hydrochloric acid, and the bismuth precipitated as oxychloride by diluting. If on dissolving the copper in nitric acid a residue remains, this should be fused with sodium carbonate and sulphur, and tested for bismuth by Hampe's method (*ibid.*, **13**, 184). The separation of arsenic and antimony from copper by conversion into iodides (Flajolot), is only satisfactory in the case of arsenic, but the addition of potassium fluoride greatly facilitates the washing out of the antimony from the cuprous iodide, owing seemingly to the formation of the highly soluble potassium antimonious fluoride. To the solution of 10 grams of copper in 50 c.c. of nitric acid of 1·4 sp. gr., after dilution to 200 or 300 c.c. with cold water, 0·15 gram of potassium fluoride is added, and then 26·2 grams of potassium iodide in small portions alternately with sulphurous acid. Excess of iodide is to be avoided. The liquid is then heated until the precipitate has completely subsided. The precipitate is washed with hot water containing sulphuric acid. After removing the excess of sulphurous acid from the filtrate by iodine, hydrogen sulphide is passed in. The precipitate is dissolved in hydrochloric acid with addition of potassium chlorate, and after adding tartaric acid and ammonia, the copper, lead, and bismuth are thrown down by the cautious addition of

dilute hydrogen sulphide, leaving the arsenic and antimony in the filtrate to be separated by the usual methods. M. J. S.

Estimation of Dissolved Carbonic Anhydride in Water. By L. VIGNON (*Compt. rend.*, **105**, 1122—1124).—50 c.c. of recently distilled water or of a well-boiled sample of the water to be tested is mixed with 10 drops of a saturated alcoholic solution of phenolphthaleïn and a standard solution of lime water is added until a pink colour is developed.

50 c.c. of the water to be tested is treated in precisely the same way, the standard solution being added until the intensity of the coloration is the same in both tubes. Towards the end of the titration, a little time must elapse between successive additions of the calcium hydroxide. The difference between the volume of alkali required in the two cases gives the amount of free carbonic anhydride.

Chlorides, sulphates, and nitrates of calcium or magnesium do not affect the result, but if the water contains magnesium carbonate, or alkaline salts the acids of which form insoluble compounds with calcium, a sufficient quantity of neutral calcium chloride should be added to convert the magnesium and the alkalis into chlorides. If the second liquid becomes so turbid that comparison of the tints is difficult, some calcium carbonate may be added to the liquid in the first tube.

This method will estimate 1 c.c. of carbonic anhydride dissolved in 1000 c.c. of water. C. H. B.

Estimation of Ash in Organic Substances. By A. KÖBRICH (*Chem. Zeit.*, **11**, 1159).—5 or 10 grams of the substance is submitted to a preliminary burning in a platinum dish, the latter being preferred to a crucible, as the chance of loss by creeping over the side is less. If the substance burns readily, the ignition is completed in the dish; if otherwise, the char is pulverised, transferred to a platinum crucible, and the ignition completed in a current of oxygen; the operation proceeds quietly without any spluttering, as is the case when ammonium nitrate is used. When particles of carbon are enclosed by the fusion of the ash, it is recommended to dissolve the mass in water; the particles of carbon rise to the surface, and after careful evaporation are easily oxidised by igniting. D. A. L.

Thiophen Reaction with Nitrous Sulphuric Acid. By C. LIEBERMANN (*Ber.*, **20**, 3231—3234).—This reaction was mentioned in 1883 (*Ber.*, **16**, 1473), but seems to have been overlooked, as one practically identical with it, has just been given by Claisen and Manasse (*Ber.*, **20**, 2197). Two or three drops of sulphuric acid containing nitrous acid are shaken for some time with 1 c.c. of the benzene under examination, when the acid gradually acquires a corn flower-blue colour. If much thiophen is present, the reaction occurs almost at once; with 2 to 3 per cent. of thiophen, it appears after a few minutes, whilst with very small quantities some 10 to 15 minutes is required for its complete development. As little as 0.25 milli-

gram of thiophen can be detected by this test. The colouring matter is precipitated on dilution with water as a deep-brown, flocculent substance, soluble in sulphuric acid, with deep-blue colour, insoluble in water. It seems to have the constitution $\text{OH}\cdot\text{N} < \begin{smallmatrix} \text{C}_5\text{SH}_2 \\ \text{C}_4\text{SH}_2 \end{smallmatrix} > \text{O}$; atmospheric oxygen is absorbed in its formation; hence the necessity of the continued shaking.

A. J. G.

Examination of Cane-sugar for Sulphurous Acid. By DAVIDSEN (*Chem. Centr.*, 1887, 1180, from *Deut. Zuckerind.*, 12, 939).—The sugar is dissolved in a few c.c. of cold very dilute starch solution. To this a few drops of iodic acid are cautiously added, so that the liquids do not mix. A blue ring appearing at the junction shows the presence of sulphurous acid (or thiosulphuric acid). This method can also be used as a quantitative one by titration with iodine.

J. W. L.

Detection and Direct Estimation of Starch in Liquids containing Dextrin. By G. BURKHARD (*Chem. Zeit.*, 11, 1158).—The liquid containing starch and dextrin is well mixed with just sufficient alcohol to produce a slight turbidity; it is then warmed until the turbidity disappears. Tannin solution is now added to this weak alcoholic solution, and when cold the starch precipitate is collected. For qualitative purposes, the precipitate can be simply tested on the filter with dilute iodine solution. For quantitative work, the tannin is washed from the precipitate by means of alcohol; the filter and precipitate are then transferred to a Lintner's pressure flask, and mixed with 20 c.c. of water and 1 c.c. of normal sulphuric acid. After heating for four hours at below 115°, the contents of the flask are neutralised with 1 c.c. of normal soda, filtered, and the sugar determined by Fehling's solution, using Allihn's tables for converting the quantity of reduced copper formed into sugar, and multiplying this figure by 0.9 to find the amount of starch present.

D. A. L.

Detection and Estimation of Aldehydes in Commercial Alcohols. By U. GAYON (*Compt. rend.*, 105, 1182—1183).—The author utilises the well-known fact that aldehydes and ketones produce a red coloration in solutions of magenta which have been decolorised by sulphurous acid.

In order to prepare the reagent, a solution of 1 gram of magenta in 1000 c.c. of water is mixed with 20 c.c. of a solution of sodium hydrogen sulphite of 30° B. After about an hour, when the liquid has become nearly colourless, 10 c.c. of pure concentrated hydrochloric acid is added. The order of mixing is important. The reagent is preserved in small, well-closed bottles, and becomes more sensitive on keeping.

The alcohol to be examined is mixed with water until its strength is approximately 50°, and 2 c.c. of the diluted liquid is mixed with 1 c.c. of the reagent. A rose-violet colour appears in a few minutes, the reaction being sufficiently delicate to detect one part of aldehyde in 500,000 parts of alcohol.

Quantitative estimations are made by comparing the depth of tint produced by the alcohol under examination with that produced by alcohol containing a known proportion of ordinary aldehyde, the results being expressed in terms of the latter. C. H. B.

Analysis of Materials containing Tartaric Acid. By N. v. LORENZ (*Zeit. anal. Chem.*, **27**, 8—14).—Goldenberg's method (*ibid.*, **22**, 270), as modified by the author, is carried out as follows:—15 grams of the finely ground substance (argol or lees) is boiled with 250 c.c. of water and 6 grams of potassium carbonate for 20 minutes with stirring, in a basin of at least 700 c.c. capacity over a free flame. After cooling, it is made up to 500 c.c. If the substance is calcium tartrate only 7.5 grams is taken, and is made up to 250 c.c. It is filtered, and 100 c.c. of the filtrate is evaporated on the water-bath as far as is possible without any salt depositing. While still hot, it is mixed with 5 c.c. of glacial acetic acid, and as soon as effervescence has ceased 100 c.c. of absolute or 95 per cent. alcohol is added. It is vigorously stirred for two minutes, allowed to remain for 15 minutes, but not longer, then the potassium hydrogen tartrate is collected by suction through a filter of 50 c.c. capacity, on which it is washed once with 50 c.c., and twice with 25 c.c. of absolute alcohol. Without drying, it is thrown with its filter into the precipitating basin, boiled with 200 c.c. of water, and titrated hot with 3/10 normal soda, boiling for five minutes, when the end is approached. A neutral decoction of litmus is used, the preparation of which is minutely described. The original solution obtained by boiling the substance with potassium carbonate must be alkaline. If, owing to the presence of much calcium sulphate, this is not the case, a fresh portion must be boiled with 12 grams of carbonate. Direct experiments show that considerable variations in the quantity of potassium carbonate used do not affect the result. On the other hand, the quantity of acetic acid prescribed must be adhered to. The 200 c.c. of alcoholic filtrate retains in solution about 0.0177 gram of potassium hydrogen tartrate, corresponding with 0.59 per cent., but this loss is to a great extent compensated for by neglecting the volume of the insoluble matter, although in the case of lees an additional 5 c.c. of water should be added in making up to partially allow for this. M. J. S.

Points of Difference between Linseed Oil and Linseed-oil Varnish. By FINKENER (*Chem. Zeit.*, **11**, 905—906).—In columns 15 mm. thick, the oil appears yellow, the varnish brown, by transmitted light. When smeared on a plate, the oil remains greasy for 24 hours, whilst the varnish becomes sticky, or even solidifies. The following test will distinguish a pure linseed oil from an oil containing 25 per cent. of the varnish. 12 c.c. of the oil under examination is shaken with 1 c.c. of a 20 per cent. solution of ammonia mixed with 5 c.c. of the test solution (composed of 100 grams of lead acetate, 150 c.c. of water, and 32 grams of glycerol), and heated at 100° for three minutes; linseed oil forms two liquid layers, the lower one clear as water; whereas linseed-oil varnish sets to a salve-like mass. So-called bleached linseed-oil varnish is paler yellow than linseed oil, neverthe-

less it resembles the latter in other points. With solvents, saponifying and oxidising agents, the behaviour of the oil is not readily distinguishable from that of the varnish. D. A. L.

Apparatus for the Estimation of Urea. By P. CAZENEUVE and HUGOUNENQ (*Bull. Soc. Chim.*, **48**, 82—86).—This apparatus consists of a copper oil-bath, provided with a thermometer and thermoregulator, and bronze tubes fitted with screw-caps, coated internally with platinum by electrolysis, and capable of withstanding a pressure of 60 atmos.

25 to 30 c.c. of the liquid to be examined is agitated with unwashed bone-black, which decolorises and neutralises it, and 10 c.c. of the filtered liquid is diluted with 20 c.c. of water, heated in one of the tubes at 180° for half an hour, and the ammonia formed is estimated by titration with normal sulphuric acid, using methyl-orange or phenolphthaleïn as indicator. The results of the test analyses given are very satisfactory. Hugounenq has previously shown that tyrosine, leucine, peptones, &c., give no ammonia when heated with water at 180—190°. C. H. B.

Note by Abstractor.—Phenolphthaleïn is useless as an indicator in presence of ammonium salts or for the titration of ammonia.—C. H. B.

Volatile Alkaloids. By O. DE CONINCK (*Compt. rend.*, **105**, 1180—1182).—A summary of the methods available for distinguishing the volatile alkaloids from one another. Details of the application of these methods will be given in a subsequent paper. C. H. B.

Inorganic Chemistry.

Specific Gravity of Sulphuric Acid Solutions. By D. MENDELÉEFF (*Zeit. physikal. Chem.*, **1**, 273—284).—The composition of the solutions is expressible by the formula $\text{H}_2\text{SO}_4 + m\text{H}_2\text{O}$; p denotes the percentage of H_2SO_4 in the solution, taking $\text{S} = 32$, $\text{O} = 16$, and s is its specific gravity. A table of the value of s derived from the researches of seven experimenters is given for different values of m . Plotting a curve, abscissæ representing the values of p , ordinates those of ds/dp , it appears that the curve consists of a number of straight lines, the discontinuities corresponding with the known hydrates. Since ds/dp is a linear function of p , an integration shows that s is a rational function of p of the second degree, the constants remaining unchanged between two consecutive discontinuities or two consecutive hydrates.

Thus for the values $m = 0, 1, 2, 6, 150$, there are discontinuities in the values of ds/dp , the first being the most considerable. The data

given are not sufficient to determine the positions of the discontinuities for $m = 6$ and $m = 150$ with accuracy. Formulæ are given for ds/dp and s in terms of p for the intervals through which these quantities are continuous, and it is shown that $ds/dp = a$ linear function of p is probably not an approximation but an exact law. The same law obtains in the case of alcohol solutions. C. S.

Pyrosulphites. By W. MEYSZTOWICZ (*Zeit. physikal. Chem.*, **1**, 73).—The failure of an attempt to prepare pyrosulphites of polyvalent metals leads the author to draw an analogy between pyrosulphurous and dichromic acids, concluding that in each the position of the hydrogen-atoms is such that they cannot be simultaneously replaced by a bivalent element. H. C.

Action of Water on Lead Pipes. By E. REICHARDT (*Arch. Pharm.* [3], **25**, 858—877).—In the vast majority of cases where lead pipes are used for domestic water supply, no injurious results follow, but in some few cases highly dangerous lead poisoning has been experienced. When lead is alternately in contact with air and water, it is rapidly attacked, and the water becomes impregnated. This solvent action is doubtless due to the oxygen of the air; but when the lead is always in contact with water only, whether under pressure or not, the presence or absence of dissolved oxygen appears to have no effect on the amount of lead dissolved. The author examined two different water supplies which caused lead poisoning where lead service pipes were employed, and compared these with several other waters which did not take up lead under similar conditions. The contaminated waters were found to contain free carbonic anhydride, that is more than was required to form bicarbonates with the bases present as carbonates, and when this free anhydride was expelled, as by boiling, or neutralised, the water no longer acted on lead. The uncontaminated waters did not contain this excess of anhydride, but on adding excess of the anhydride the waters became capable of dissolving lead (compare (Müller, this vol., p. 225). J. T.

Tungsten Compounds. By W. FEIT (*Ber.*, **21**, 133—137).—By the reduction of a fused mixture of sodium and potassium tungstates with tin, the author obtains the compounds $3K_2W_4O_{12} + 2Na_2W_3O_9$, and $5K_2W_4O_{12} + 2Na_4W_6O_{15}$, prepared by v. Knorre (Abstr., 1883, 650, 651), and also a compound which probably has the formula $K_2W_4O_{12} + Na_2W_5O_{15}$. The author has endeavoured to prepare corresponding compounds of lithium. By reducing a fused mixture of sodium tungstate and lithium tungstate with tin, three compounds are obtained, a deep blue lithium compound (probably $Li_2W_5O_{15}$) and two sodium compounds, one of which seems to be the compound $Na_5W_6O_{18}$. A homogeneous product, $Li_2W_3O_{15} + 3K_2W_4O_{12}$, crystallising in violet needles, is obtained by reducing a mixture of potassic tungstate (one mol.), and lithium tungstate (one mol.). As the proportion of base and acid (3 : 7 or 5 : 12) in the paratungstates of the light metals can scarcely be proved by analysis, the

difference being too small, the author intends to prepare the salts of some metals of a high atomic weight. J. W. L.

Boiling Point and Molecular Formula of Stannous Chloride.

By H. BILTZ and V. MEYER (*Ber.*, **21**, 22—24).—The boiling point of stannous chloride is found to be 606.1° , as a mean of two series of experiments.

The vapour-density of this salt diminishes only very gradually with an increase of temperature, so that it must be heated hundreds of degrees above its boiling point in order to obtain numbers agreeing with the molecular formula SnCl_2 . The determinations made at temperatures less than 100° above the boiling point show that the view of V. and C. Meyer, that at low temperatures the molecular formula is Sn_2Cl_4 , cannot be upheld; for although at relatively low temperatures values are obtained which are greater than those corresponding to SnCl_2 , no constant results could be obtained which would lead to the doubled formula. F. S. K.

New Source of Germanium. By G. KRÜSS (*Ber.*, **21**, 131—133).

—The author finds that germanium is contained in euxenite to the amount of 0.1 per cent., and that it replaces titanium in this mineral. He intends to examine other minerals, such as rutile, yttrotitanite, wöhlerite, &c., for germanium. J. W. L.

Atomic Weight of Gold. By G. KRÜSS (*Ber.*, **21**, 126—130).—

A controversial paper in reply to Thorpe and Laurie (*Trans.*, 1887, 565, 866).

Mineralogical Chemistry.

An English Coal. By SCHEURER-KESTNER and MEUNIER-DOLFUS (*Compt. rend.*, 105, 1251—1255).—The coal was obtained from Glamorganshire. It gave 88 per cent. of coke and 3 to 4 per cent. of ash, the composition being as follows:—C 90·27, H 4·39, S 0·69, N 0·49, O 4·16. The composition of the volatile portion was C 22·53, H 34·96, O + N + S 42·51. The heat of combustion as actually determined (8864 cal.) differs considerably from that calculated by means of any of the usual formulæ. C. H. B.

Artificial Pyrochroite. By A. DE SCHULTEN (*Compt. rend.*, 105, 1265—1267).—300 grams of pure potassium hydroxide was dissolved in 500 c.c. of water, boiled for some time in a flask through which a current of hydrogen or coal gas was passing, and a recently boiled solution of 15 to 17 grams of crystallised manganous chloride in 15 c.c. of water was introduced by means of a funnel with a stopcock. The flask was then heated to about 160°, when the whole of the manganous hydroxide dissolved. As the liquid cools, it deposits crys-

tallised manganous hydroxide, and becomes almost solid. The crystals are washed with recently boiled water, alcohol, and ether, and dried at a gentle heat in a current of hydrogen. If sodium hydroxide is used, the precipitate does not dissolve even in concentrated solutions at 200°, but it becomes crystalline. Crystallised manganous hydroxide dissolves readily in hydrochloric acid and in a solution of ammonium chloride. When heated to redness in the air, it forms manganoso-manganic oxide, which retains the form of the original crystals. When heated in hydrogen, it yields manganous oxide, which is green when hot and grey when cold.

Manganous hydroxide under these conditions crystallises in flattened, transparent, regular, hexagonal prisms, with a reddish tint. The crystals are uniaxial, and the axis is negative, as in pyrochroite. Crystallised cadmium hydroxide likewise has a negative axis, but magnesium hydroxide, natural or artificial, has a positive axis. When the manganous hydroxide is pure, it alters very slowly in presence of air, but if it contains even a small quantity of alkali, it oxidises very quickly.

C. H. B.

Mineralogical Notes. By G. F. KUNZ (*Amer. J. Sci.*, **34**, 477—480).—1. *Rhodochroisite from Colorado*.—Rhodochroisite, in rich, red, transparent rhombohedra, has been found in the John Reed Mine at Alicante, Lake Co., Colorado. This is the first locality that has yielded crystals of such size (12 mm. across) and transparency. The sp. gr. is 3.69, and the hardness 3.5. Analysis gave the following results:—

MnO.	FeO.	CaO.	MgO.	CO ₂ .	Total.
38.35	3.61	nil	trace	(38.96)	100.00

2. *Hollow Quartz Crystals from Arizona*.—These crystals are found about 3 miles south-west of the town of Pinal, Pinal Co., Arizona. They occur in sandstone, penetrated in many places by spherules of obsidian. The crystals are mere walls surrounding hollow spaces much larger than the area of the wall itself.

3. *Hydrophane from Colorado*.—A white, opaque variety of hydrophane in rounded lumps, 5 to 25 mm. in diameter, has recently been brought from Colorado. It is remarkable for its power of absorbing water. When water is allowed to slowly drop on it, it first becomes white and chalky, and then gradually perfectly transparent. It was found by weighing that this mineral absorbs more than an equal volume of water.

4. *A Remarkable Nugget of Silver*.—One of the most remarkable nuggets of silver known was found in limestone at the Greenwood Mines in the State of Michoacan, Mexico. It weighed 606½ oz., and in its original state weighed 12 lbs. more. It consists of almost pure silver, and is entirely worn except in cavities where the form of some of the crystals is still visible.

B. H. B.

Bismuthosphærite from Willimantic and Portland, Connecticut. By H. L. WELLS (*Amer. J. Sci.*, **34**, 271—274).—The author has examined two specimens of basic bismuth carbonate, the composition of which appears to be identical with that of Weisbach's

bismuthosphærite. The composition of that mineral has been considered doubtful by A. H. Chester (Abstr., 1887, 783), because no water was included in the analysis. In the Connecticut specimens, the percentage of water did not exceed 0.94. Since a part of the water found was probably hygroscopic moisture, and since the determinations were made by weighing the water in a calcium chloride tube, a method apt to give slightly high results, these two specimens of bismuth carbonate must be regarded as anhydrous. The analyses agree closely with the formula $\text{Bi}_2\text{O}_3\cdot\text{CO}_2$. The existence of bismuthosphærite must thus be considered as established. B. H. B.

Natural Borates and Borosilicates. By J. E. WHITFIELD (*Amer. J. Sci.*, **34**, 281—287).—The author has repeated the analyses of some natural borates, in order to correct errors due to defective analytical methods. The boric acid was determined by the method devised by F. A. Gooch (Abstr., 1887, 299).

Colemanite from Death Valley, California, gave on analysis the following results:—

H_2O .	B_2O_3 .	CaO .	MgO .	Total.
21.87	50.70	27.31	0.10	99.98

These results correspond with the formula $2\text{CaO}\cdot 3\text{B}_2\text{O}_3\cdot 5\text{H}_2\text{O}$. The same formula was calculated by J. T. Evans (Abstr., 1885, 958), from his analysis, in which the boric acid was determined by difference.

Priceite from Curry Co., Oregon, gave the following composition:—

H_2O .	B_2O_3 .	CaO .	Total.
19.42	48.44	32.15	100.01

Pandermite from Panderma, in the Black Sea, gave on analysis the following results:—

H_2O .	B_2O_3 .	CaO .	Total.
19.40	48.63	32.16	100.19

It will thus be seen that priceite and pandermite are identical in composition. The difference is solely in the physical character of the minerals, priceite being soft and friable, and pandermite hard and compact (compare Abstr., 1885, 1117).

Uleinite from Rhode's Marsh, Esmeralda Co., Nevada, gave on analysis the following figures:—

SiO_2 .	Cl.	B_2O_3 .	SO_3 .	CaO .	Na_2O .	K_2O .	H_2O .	Total.
0.04	2.38	43.20	0.28	14.52	10.20	0.44	29.46	100.52

The analysis being corrected for impurities, the formula $\text{NaCaB}_2\text{O}_6 + 6\text{H}_2\text{O}$ is deduced.

Ludwigite from Moravitz, in the Banat, gave on analysis the following results:—

B_2O_3 .	Fe_2O_3 .	FeO .	MgO .	MnO .	H_2O .	Total.
12·04	37·93	15·78	30·57	0·16	3·62	100·10

Tschermak obtained 16·09 per cent. of boric acid, but gives no water.

Datolite from Bergen Hill, New Jersey, gave—

SiO_2 .	FeO .	CaO .	B_2O_3 .	H_2O .	Total.
35·74	0·31	35·14	22·60	6·14	99·93

The formula is thus $B_2O_3, H_2O, 2CaO, 2SiO_2$.

Danburite from Russell, St. Lawrence Co., New York, gave—

SiO_2 .	B_2O_3 .	CaO .	$Fe_2O_3 + Al_2O_3$.	Ign.	Total.
49·70	25·80	23·26	1·02	0·20	99·98

Axinite from Cornwall (I), and from Bourg d'Oisans, Dauphiné (II), gave on analysis the following results:—

	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	CaO .	MnO .	MgO .	B_2O_3 .	H_2O .	Total.
I.	42·10	17·40	3·06	5·84	20·53	4·63	0·66	4·64	1·80	100·66
II.	41·53	17·90	3·90	4·02	21·66	3·79	0·74	4·62	2·16	100·32

The formula is $BR'''_3R''_4H_2(SiO_4)_6O$.

B. H. B.

Pseudomorphs in the Lead Mines of the Puy de Dome.

By F. GONNARD (*Compt. rend.*, 105, 1267—1269).—The enveloping pseudomorphs or perimorphoses consist of thin coatings of one mineral on the crystals of another. In the lead mines of the Puy de Dome, enveloping pseudomorphs of pyromorphite on cerussite or galena are frequently observed. Sometimes the mineral inside has undergone alteration, owing to the fact that the envelope has not protected it from the air, &c. Not unfrequently, when the layer of pyromorphite is of appreciable thickness, it is distinctly crystalline, and the hexagonal prisms can readily be recognised. It is obvious that an envelope of this character is not a true pseudomorph.

Another mineral found in the form of enveloping pseudomorphs is siderite. One specimen showed the unusual form of hexagonal prisms surmounted by rhombohedrons. Calcite does not occur associated with it, and hence it cannot be regarded as a pseudomorph after that mineral. The nature of the original mineral was not determined. The form is, however, possible for any substance crystallising in the rhombic system, and hence this is a case of siderite occurring as a pseudomorph under a form in which it might crystallise itself.

Pseudomorphs of pyrites on calcite were also found, the envelope of pyrites being crystalline, and showing combinations of the cube with the pentagonal dodecahedron.

C. H. B.

Crystalline Compounds prepared by Ebelmen. By E. MALLARD (*Compt. rend.*, 105, 1260—1265).—*Artificial phenacite*, $SiO_2, 2BeO$, obtained by fusing beryllia and silica with borax, forms

small, regular, hexagonal prisms with very brilliant faces, the optical sign being positive.

Beryllium chromite, $\text{BeO}, \text{Cr}_2\text{O}_3$, prepared by fusing chromic oxide with beryllia and boric anhydride, is a deep green powder, which polarises strongly under the microscope, and consists of minute crystals of a form identical with that of the variety of cymophane known as alexandrite. It is therefore analogous to the corresponding aluminium compound, the artificial cymophane likewise obtained by Ebelmen.

Crystallised niobic anhydride forms small, rhombic prisms with two perpendicular cleavages, h' and g' , the angle mm being $140^\circ 50'$, and the horizontal parameters $0.355 : 1$. The form seems to be pseudo-cubic; the acute positive bisectrix is perpendicular to h' , the plane of the axes being p .

Tantalalic anhydride was obtained in rhombic prisms with the faces $g' h'$ well developed, and the subordinate faces m, g^2, g^3, g^5 , the angle mm being about 143° . It follows that niobic and tantalalic anhydrides are isomorphous.

Crystallised beryllia has the parameters $a : h = 1 : 1.6305$, the optical sign being positive. In crystallised zinc oxide, the parameters are $a : h = 1 : 1.6034$, and the optical sign is likewise positive. It follows that these two oxides are isomorphous, notwithstanding the difference in their specific volumes.

Aluminium borate, $\text{B}_2\text{O}_3, 3\text{Al}_2\text{O}_3$, which Ebelmen analysed but did not describe, crystallises in rhombic needles, the dominant face being m truncated by g' and h' ; angle $mm = 91^\circ 21'$; acute positive bisectrix parallel with the vertical, the plane of the axes being parallel with g' .

The compound $3\text{B}_2\text{O}_3, 2\text{Fe}_2\text{O}_3, 9\text{MgO}$, which Ebelmen analysed, forms black, opaque prisms, which have very brilliant faces, and probably belong to the rhombic system. The principal faces are m and h' , the angle mm being $90^\circ 32'$. An analogous compound containing chromium in place of iron forms a dark brown powder consisting of small prisms, which when examined by polarised light seem to belong to the rhombic system.

Ebelmen prepared crystallised tribasic borates, $\text{B}_2\text{O}_3, 3\text{RO}$, which on his assumption that boric acid is analogous to silicic acid, are analogous to peridot, the oxygen ratio being $1 : 1$; and likewise crystallised sesquibasic borates, which on the same assumption are analogous to enstatite. The tribasic borates actually obtained were the magnesium, manganese, and cobalt compounds. They are isomorphous, and belong to the rhombic system, the parameters being as follows:—

$\text{B}_2\text{O}_3, 3\text{MgO}$	$0.6412 : 1 : 0.5494$	$mm = 114^\circ 40'$
$\text{B}_2\text{O}_3, 3\text{CoO}$	$0.6461 : 1 : ?$	$mm = 114 \ 15$
$\text{B}_2\text{O}_3, 3\text{MnO}$	$0.6511 : 1 : 0.5351$	$mm = 113 \ 52$

The faces m are faces of cleavage, and the acute positive bisectrix is parallel with the vertical, the plane of the axes being g' . The principal indices of refraction for D are respectively $1.6748, 1.6537, 1.6527$.

The sesquibasic borates obtained are the magnesium, manganese,

and zinc compounds. They are isomorphous, and belong to the triclinic system, the parameters of the manganese compound being $1.8373 : 1 : 2.012$, and $xy = 76^\circ 26'$, $xz = 123^\circ 58'$, $yz = 92^\circ 6'$, $g'h' = 75.01$, $ph' = 124^\circ 29'$, $pg' = 83^\circ 16'$. All have easy nacreous cleavage along p , and a less easy vitreous cleavage along t . The nacreous cleavage is almost always perpendicular to an optical axis. C. H. B.

Triclinic Felspars with Twinning Striations on the Brachypinacoid. By S. L. PENFIELD and F. L. SPERRY (*Amer. J. Sci.*, **34**, 390—393).—The authors give the results of a careful study, in connection with the chemical composition of the felspars, of the striations due to twinning on $\infty P\infty$ exhibited by very many cleavage specimens of plagioclase felspar, in addition to the ordinary striations on the basal plane. These striations on $\infty P\infty$ have been shown by G. v. Rath (*Abstr.*, 1878, 713) to have resulted from twinning according to the pericline law. The two individuals are united by a plane deviating slightly from the basal plane, passing through the macro-axis, and so inclined that the four plane angles it makes with the prisms ∞P and $\infty P'$ and the pinacoid $\infty P\infty$ are all equal. This is the so-called rhombic section. Owing to the variations in the axial angles of anorthite felspars, the direction of the rhombic section changes considerably. The direction above the line parallel to the edge $OP : \infty P\infty$ being regarded as positive, and that below as negative, the direction of the rhombic section in felspars of the albite-anorthite group was found by Tschermak to be as follows:—

			Na ₂ O per cent.	CaO per cent.
Albite, Na ₂ Al ₂ Si ₆ O ₁₆ ..	Ab	+22°	11.8	0.0
Oligoclase	Ab ₃ An ₁	+ 4	8.7	5.2
Andesine	Ab ₁ An ₁	— 2	5.7	10.4
Labradorite	Ab ₁ An ₃	— 9	2.8	15.3
Anorthite, Ca ₂ Al ₄ Si ₄ O ₁₆	An	—18	0.0	20.1

	1.	2.	3.	4.	5.	6.
SiO ₂	66.58	66.83	66.06	66.34	65.73	63.76
Al ₂ O ₃	21.26	20.88	21.57	20.72	21.32	22.67
Fe ₂ O ₃	0.07	0.25	0.18	—	0.12	0.41
CaO	1.18	1.46	1.80	1.85	1.95	3.05
Na ₂ O	10.26	10.36	9.57	9.44	9.66	6.89
K ₂ O	0.76	0.70	1.01	0.98	0.95	3.60
Ignition	0.16	0.27	—	0.38	0.19	0.40
Total	100.27	100.75	100.19	99.71	99.92	100.78
Sp. gr.	2.610	2.632	2.633	2.627	2.628	2.622
Ratio An : Ab	1 : 16.0	1 : 13.0	1 : 9.6	1 : 9.2	1 : 9.0	1 : 4.1
Anorthite per cent. ..	5.87	7.25	8.94	9.20	9.70	15.17
Rhombic section ...	+12°	14°	13°	12°	10°	10°
Extinction on $\infty P\infty$..	15	15	16	12	15	6°

In order to show the relation between the direction of the striations and the chemical composition of the feldspars, the authors made analyses of cleavage specimens from six different localities, namely: 1, Branchville, Connecticut; 2, Hitterö, Norway; 3, Haddam, Connecticut; 4, Mineral Hill, Pennsylvania; 5, Danbury, Connecticut; 6, Pierrepont, New York. All the specimens show distinct striations on $\infty\bar{P}\infty$, and all satisfy Tschermak's formula as mixtures of $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16}$ and $\text{Ca}_2\text{Al}_4\text{Si}_4\text{O}_{16}$. The analytical results are given on the preceding page.

Judging from the above, it will be safe to predict that where the striations on $\infty\bar{P}\infty$ make an angle of about $+12^\circ$, the feldspar will be a mixture of albite with 5 to 10 per cent. of anorthite.

The authors have been unable to find many specimens of feldspars more basic than oligoclase exhibiting striation on $\infty\bar{P}\infty$. The analysis of a specimen of labradorite from Labrador gave results in very satisfactory accord, both as regards the direction of the rhombic section and the extinction angle on $\infty\bar{P}\infty$, with the table given by Tschermak. Although the variation in the angles of plagioclase crystals is considerable, the change in position of the rhombic section from $+22^\circ$ to -18° is so great that the direction of the striations will clearly indicate what position any plagioclase holds in the albite-anorthite series.

B. H. B.

So-called Indicolite from Harlem. By R. B. RIGGS (*Amer. J. Sci.*, **34**, 406).—A peculiarly bright blue mineral found at Harlem, New York, was supposed to be the rare variety of tourmaline known as indicolite. An analysis made by the author showed relations very different from those in tourmaline, the analytical results being as follows:—

SiO_2 .	B_2O_3 .	Al_2O_3 .	MgO .	Na_2O .	K_2O .	Ignition.	Total.
34.82	4.07	55.30	0.57	1.76	1.04	2.96	100.52

The molecular ratios, deduced from the analysis, are closely expressed by the formula $3\text{H}_2\text{O}, (\text{Na}, \text{K})_2\text{O}, 10\text{Al}_2\text{O}_3, 10\text{SiO}_2, \text{B}_2\text{O}_3$, a new borosilicate. A microscopic study of this blue mineral shows that the angle of extinction is very small. The mineral is undoubtedly biaxial with remarkable pleochroism (ultramarine, reddish-violet, colourless). Its structure is subfibrous, so as to render the angle of prismatic cleavage somewhat obscure. It is thus certain that the blue mineral is not indicolite, but in all probability a new borosilicate.

B. H. B.

Remarkable Crystals of Pyroxene from New York. By G. H. WILLIAMS (*Amer. J. Sci.*, **34**, 275—276).—Some yellowish-grey crystals of pyroxene occurring in the crystalline limestone of Orange Co., New York, have a peculiar tabular habit produced by the unusual development of the basal pinacoid. A remarkably fine group of these crystals, in the collection of the Johns Hopkins University, exhibits great singularity of form. It consists of six simple tabular crystals, and of two larger ones, which are at the same time twins and hemimorphic. The largest of these crystals measures 3 by $3\frac{1}{2}$ cm. The upper portion shows the usual forms: 0P , $-\text{P}$, P , 2P , ∞P , $\infty\text{R}\infty$,

$\infty\bar{P}\infty$. Below, however, towards the front, there are only the forms 2P and $\bar{P}\infty$, indicating that the crystal is hemimorphic in the direction of the vertical axis. The lower back quarter of the crystal is exactly like the lower front quarter, but in a reversed position, so that the lower half of the crystal is a twin. The second crystal is essentially the same as the one just described. B. H. B.

Blue Clay from Farmington, Maine. By F. C. ROBINSON (*Amer. J. Sci.*, **34**, 407—408).—An analysis of blue clay from Farmington, Maine, gave the following results:—

SiO ₂ .	Al ₂ O ₃ .	FeO.	CaO.	Na ₂ O.	H ₂ O.	Total.
63·69	17·02	10·18	0·97	4·02	4·05	99·93

An approximate mechanical analysis gave the following percentages:—

Coarse sand.	Fine sand.	Fine clay.	Water.
3·73	22·97	69·25	4·05

The sand consisted principally of felspar, with traces of quartz and mica. The clay is used for brickmaking. B. H. B.

Meteorite from St. Croix Co., Wisconsin. By D. FISHER (*Amer. J. Sci.*, **34**, 381—383).—The mass of meteoric iron described was ploughed up in 1884 on a farm in Hammond Township. It weighed 53 lbs., and measured 8 by 8 inches across the face, with an average thickness of 5 inches. The character of the meteorite renders it probable that its fall did not precede the date of its discovery by many months. An analysis of the meteorite gave the following results:—

Fe.	Ni.	Co.	P.	SiO ₂ .	Total.	Sp. gr.
89·78	7·65	1·32	0·51	0·56	99·82	7·60—7·70

with traces of carbon, copper, and tin. Troilite is present in nodules 5 to 10 mm. in size. On the application of dilute nitric acid, the Widmanstätten figures quickly appear. These are cubical in arrangement. The meteorite now forms part of the Yale University collection at New Haven. B. H. B.

The Rockwood Meteorite. By J. E. WHITFIELD (*Amer. J. Sci.*, **34**, 387—390).—This meteorite was found in March, 1887, in a field $8\frac{1}{2}$ miles west of Rockwood, Tennessee. Three pieces were found. The smallest measured 4 by 3 by $2\frac{1}{2}$ inches, and weighed 3 lbs. $10\frac{1}{2}$ oz.; the next measured $7\frac{7}{8}$ by $6\frac{1}{2}$ by $2\frac{3}{8}$ inches, and weighed 5 lbs. $13\frac{1}{2}$ oz.; and the largest measured $14\frac{3}{4}$ by 10 by $8\frac{1}{2}$ inches, and weighed 85 lbs. The mass is very brittle. Cut slices show irregularly shaped stony fragments, with metallic grains distributed through the mass. An analysis of the metallic portion gave 87·59 per cent. of iron, 12·09 per cent. of nickel, with traces of cobalt and copper, but

neither phosphorus nor sulphur. An analysis of the stony portion gave the following results:—

SiO ₂ .	Al ₂ O ₃ .	FeO.	CaO.	MgO.	Fe.	Ni.	Cl.	P.	S.	Total.
41.92	9.27	22.94	9.09	8.76	3.75	1.74	0.18	0.65	1.58	99.88

This meteorite appears to be a lithosiderite poor in metal, the metallic portion not exceeding 16 per cent. of the mass. The stony part is probably anorthite and enstatite. B. H. B.

The Powder Mill Creek Meteorite. By G. F. KUNZ (*Amer. J. Sci.*, **34**, 476—477).—This meteorite is identical with the Rockwood meteorite (see preceding Abstract), and has been called from the Powder Mill Creek, because it fell in Cumberland Co.; Roane Co. in which Rockwood is situated being adjacent to this. The author is the possessor of a piece weighing 2000 grams. It resembles very closely the Hainholz, Westphalia, and the Taney Co., Missouri, meteorites. Its sp. gr. is 4.745. Chloride of iron (lawrencite) is present in considerable quantities. Under the microscope, clear crystals of anorthite and olivine were seen in the ground-mass of metallic iron. B. H. B.

Some American Meteorites. By G. F. KUNZ (*Amer. J. Sci.*, **34**, 467—477).—1. *The Taney Co., Missouri, Meteorite.*—This is supposed to have fallen in 1857 at a spot near Miney in Taney Co., 11 miles south-east of Forsyth. It was taken 60 miles to a farm in Limestone Valley, Arkansas, on the supposition that it was of value. In June, 1887, it came into the author's possession. It measures 34 by 35 by 29 cm. Its weight is 89.796 kilos. It is similar to the Hainholz, Westphalia, iron, and belongs to the logronite group of Mennier and the syssidères of Daubrée. Two large crystals of olivine are present, and at one corner of the mass there is a large inclosure of augite. The surface of the meteorite is deeply pitted, and exhibits traces of a black crust. An analysis of the metallic portion gave—

Fe.	Ni.	Co.	P.	Total.
89.41	10.41	0.29	0.16	100.27

The analysis of the stony portion gave—

SiO ₂ .	Al ₂ O ₃ .	FeO.	CaO.	MgO.	NiS.	FeS.	Total.
45.88	7.89	19.73	6.02	17.96	1.67	0.54	99.69

Further analyses of the finely ground stony portion show that the insoluble portion is enstatite only, and that the soluble portion is a lime-iron silicate containing 17 per cent. of alumina. The fragments described by C. U. Shepard (*Amer. J. Sci.*, **30**, 1860, 205) as the Forsyth iron, and by J. L. Smith (*ibid.*, **40**, 1865, 213) as the Newton Co., Arkansas, meteorite, are undoubtedly parts of the same meteorite which originally fell near Miney, in Taney Co.

2. *The Chattooga Co., Georgia, Meteorite.*—This mass was found on March 27th, 1887. In all, 12.5 kilos. were found. It is one of the

caillite group of Meunier, and has a sp. gr. of 7·615. Analysis gave the following results:—

Fe.	Ni.	Co.	P.	Total.
94·60	4·97	0·21	0·21	99·99

This iron does not bear the slightest resemblance to either of the Whitfield Co., Georgia, irons, found in the vicinity. It is a white iron, whilst the Walker Co., Alabama, iron has a bluish tinge and was found 100 miles due east.

3. *Meteorite Iron from Waldron Ridge, Claiborne Co., Tennessee.*—This was found in March, 1887, and supposed to be iron ore. The meteorite is one of the caillite group of Mennier. On the largest piece, weighing 15 lbs., the octahedral structure is very marked. The smaller pieces, weighing collectively several pounds, show considerable weathering. The iron separates readily at the cleavage plates, between which are thin leaves of schreibersite. Troilite and graphite were also observed. It thus appears that this meteorite is identical with the Cosby Creek, Cocke Co., the Sevier Co., the Greenbrier Co., and the Jennies Creek meteorites, which, although independently described, have been shown by Huntington to be parts of one meteorite.
B. H. B.

Phosphatic Mineral Water. By BOURGOIN and CHASTAING (*J. Pharm.* [5], 16, 337—341).—At Viry (Seine-et-Oise) is a spring found in a gallery cut in clay. The temperature of the water is constant at 4° even in summer, the yield is about 14 litres per minute, and though quite limpid at first a deposit is quickly formed.

A litre of water was found to contain—

Carbonic anhydride	0·17096 or 86·49 c.c.
Tricalcium phosphate	0·17901
Calcium hydrogen carbonate....	0·21740
Magnesium hydrogen carbonate	0·03640
Calcium nitrate	0·04100
„ sulphate	0·05364
Sodium chloride	0·04130
Potassium chloride.....	traces
Lithium	sensible quantity
Silica	0·01980
Organic matter	0·00200
	<hr/>
	0·76151

In an open flask, beautiful, lamellar crystals form after some days, which seem to be composed of calcium phosphate, and the water, originally acid, becomes sensibly neutral.
J. T.

Composition of Certain Colliery Waters. By P. P. BEDSON (*J. Soc. Chem. Ind.*, 6, 712—715).—The author gives the results, expressed in grams per litre, of the analyses of two colliery waters:—

	FeSO ₄ .	BaCl ₂ .	CaCl ₂ .	MgCl ₂ .	LiCl.	NaCl.	CaSO ₄ .
I.	—	1·372	21·058	3·127	0·358	59·265	—
II.	1·080	—	20·021	2·770	53·530		0·620
		CaCO ₃ .	MgCO ₃ .	Total.			
	I.	—	—	85·180			
	II.	0·134	0·021	78·176			

I. Water from the Redheugh Colliery. This water drains from the Brockwell seam and adjacent rock. Temperature 13°. II. Water from the Wardley Colliery. This water is remarkable not only from its mineral constituents but also from the fact that it contains a large amount of gas dissolved in it.

The analysis of the gas showed it to have the following composition :—

CO ₂ .	CH ₄ .	N.	
81·14	5·20	13·29	D. B.

Organic Chemistry.

Constitution of Nitroethane. By G. GÖTTING (*Annalen*, **243**, 104—131).—By the action of ethyl iodide on nitroethane and sodium ethoxide in sealed tubes at 100°, a liquid of the composition C_5H_7NO is produced. It boils at 166—170° and is freely soluble in alcohol and ether. At a higher temperature, it decomposes, yielding pyridine and a resinous residue. Sodium iodide, sodium nitrite, and ammonium iodide, are formed as bye-products when ethyl iodide acts on sodium nitroethane. The nitrite and ammonium iodide are probably formed by secondary reactions. The primary reaction may be represented by the equation $9C_2H_5NO_2 + 6EtI + 6C_2H_5ONa = 6C_5H_7NO + 6C_2H_5OH + 9H_2O + 6NaI + 3NH_2OH$.

By substituting methyl, propyl and isobutyl iodides for ethyl iodide in the preceding experiment a series of homologous compounds is obtained having the composition—

	Boiling points.
C_4H_5NO	150—160°
C_5H_7NO	166—170
C_6H_9NO	175—178
$C_7H_{11}NO$	182—185

Each of the compounds is decomposed by distillation, yielding a volatile base. The formation of C_5H_7NO and its homologues can be more readily explained by Geuther's assumption that nitroethane is in reality acetamidoxide, $CH_3CO \cdot NH_2O$, than by V. Meyer's formula $CH_3CH_2NO_2$.

W. C. W.

Preparation of Hydrosulphides and Sulphides of Methyl and Ethyl. By P. KLASON (*Ber.*, **20**, 3407—3413).—Methyl hydrogen sulphide is prepared by diluting with ice a cold mixture of 750 c.c. of sulphuric acid and 500 c.c. of absolute methyl alcohol, and adding the whole to a solution of 2.75 kilos. of crystallised sodium carbonate. The solution is concentrated to such an extent that most of the sodium sulphate separates. The mother-liquor is then concentrated, mixed with a solution of 500 grams of potash in 1 litre of water, previously saturated with hydrogen sulphide, and heated on a water-bath. The gases evolved are passed first through a strong aqueous solution of 50 grams of potash, and then into a solution of 350 grams of potash in 700 c.c. of water. The small amount of hydrogen sulphide contained in the latter solution is precipitated with lead acetate, and the ethyl hydrogen sulphide liberated by the addition of hydrochloric acid. It is dried with potash and distilled. 500 c.c. of alcohol yielded about 200 grams of methyl hydrogen sulphide, and 40 grams of methyl sulphide. It is a thin, colourless, refractive liquid, having a very repulsive odour; it boils at 5.8° under 752 mm. pressure, and yields a crystalline hydrate with water (compare Gregory, *Annalen*, **15**, 239; and Obermeyer, this vol., p. 124).

Mercury methyl mercaptide, $\text{Hg}(\text{SMe})_2$, is best prepared by passing methyl hydrogen sulphide through an aqueous solution of mercury cyanide; it is almost insoluble, and melts at 175° . The *lead compound*, $\text{Pb}(\text{SMe})_2$, forms microscopic, crystalline plates; it is decomposed by exposure to air or light. The *bismuth compound*, $\text{Bi}(\text{SMe})_3$, crystallises in yellow, microscopic needles; the *silver compound* forms a yellow, crystalline precipitate.

Ethyl hydrogen sulphide is prepared similarly to the methyl compound, using 1 litre of absolute alcohol, 500 c.c. of sulphuric acid, 4 kilos. of sodium carbonate, and 800 grams of potash. *Copper ethyl mercaptide*, CuSEt , not $\text{Cu}(\text{SEt})_2$, is readily obtained when the mixed solutions of copper sulphate and sodium acetate are treated with ethyl hydrogen sulphide, and forms a pale yellow, amorphous powder. It was previously stated (*J. pr. Chem.* [2], **15**) that zinc and cadmium mercaptides are not decomposed by hydrochloric acid; later experiments show that all mercaptides with a positive metal are decomposed by hydrochloric acid.

Methyl sulphide is prepared by distilling a concentrated solution of methyl sodium sulphate (from $\frac{1}{2}$ litre of absolute methyl alcohol) with an aqueous solution of 500 grams of potash, previously half saturated with hydrogen sulphide. The yield is 150 grams. It boils at 37.2° under 758 mm. pressure. Ethyl sulphide may be prepared in a similar manner, and boils at 91.9° . Methyl ethyl sulphide is prepared by distilling a solution of methyl hydrogen sulphide (from 250 c.c. of alcohol) in potash with sodium ethyl sulphate (from 550 c.c. of alcohol); it boils at 66.9° . The yield was 160 grams.

N. H. M.

Alkyl Polysulphides. By P. KLASON (*Ber.*, **20**, 3413—3415).—When methyl hydrogen sulphide is passed into 100 grams of sulphur chloride, (S_2Cl_2), a product is obtained free from chlorine, probably consisting of methyl tetrasulphide, methyl trisulphide, and sulphur.

When distilled in a vacuum, methyl trisulphide passes over, and sulphur remains. Methyl trisulphide (Cahours, *Annalen*, **61**, 92) is a pale-yellow oil of a very disagreeable odour, boiling at 170° with slight decomposition. In a vacuum, it distils at 62° . Sp. gr. = 1.2162 at 0° ; 1.2059 at 10° ; and 1.119 at 17° (compared with water at 0°).

Paratolyl hydrogen sulphide reacts with sulphur chloride, yielding Otto's paratolyl tetrasulphide (*Abstr.*, 1887, 954). N. H. M.

Sulphines and the Valency of Sulphur. By H. KLINGER and A. MAASEN (*Annalen*, **243**, 193—218).—The authors have repeated Krüger's experiments (*this Journal*, 1877, i, 186) on isomeric sulphine compounds, and they prove that the diethylmethylsulphine iodide, prepared by the action of methyl iodide on diethyl sulphide, is identical with the product of the action of ethyl iodide on methyl ethyl sulphide. This is shown by an examination of the platino-, auro-, and mercurio-chlorides, and also of the cadmio-iodide.

Dimethylethylsulphine iodide, SMe_2EtI , is formed not only by the action of methyl iodide on ethyl methyl sulphide, but also by the action of methyl sulphide on ethyl iodide. It is a hygroscopic, crystalline substance, soluble in alcohol, and is precipitated from the alcoholic solution by ether. It melts at $108\text{--}110^{\circ}$. The *cadmio-iodides*, $2\text{SMe}_2\text{EtI}, \text{CdI}_2$, melting with slight decomposition at 179° , and $\text{SMe}_2\text{EtI}, \text{CdI}_2$, melting at $98\text{--}99^{\circ}$, were prepared. The *mercurio-chlorides*, $\text{SMe}_2\text{EtCl}, 2\text{HgCl}_2$ and $\text{SMeEt}_2\text{Cl}, 6\text{HgCl}_2$, melt at 118° and 200° respectively. The *platinochloride*, $2\text{C}_4\text{H}_{11}\text{SCl}, \text{PtCl}_4$, forms orange-red crystals belonging to the regular system. It is insoluble in alcohol and ether. The *aurochloride*, $\text{C}_4\text{H}_{11}\text{SCl}, \text{AuCl}_3$, forms minute crystals melting at $240\text{--}244^{\circ}$.

As the supposed existence of Krüger's isomeric sulphines forms the sole argument in favour of the view that the four affinities of the sulphur-atom are of dissimilar nature, the author's results show that there is no longer any experimental evidence in support of this hypothesis. W. C. W.

Disulphones. By E. FROMM (*Ber.*, **21**, 185—188).—When brom-ethylidenediethylsulphone (*Abstr.*, 1887, 123) is heated with aqueous potash, it is converted into ethylidenediethylsulphone; the yield, however, does not amount to that theoretically possible, and inasmuch as sulphuric acid is one of the products of the reaction, it is probable that hydroxyethylidene disulphone is formed, but acting as an oxidising agent is itself reduced to ethylidenedisulphone.

When ethylidenediethylsulphone, which melts at $75\text{--}78^{\circ}$ and not at 60° , as stated by Escales and Baumann (*ibid.*), is dissolved in anhydrous ether or benzene, and treated with sodium, hydrogen is evolved and a compound obtained which could not be purified; diethylsulphonedimethylmethane (Baumann, *ibid.*) is, however, obtained if methyl iodide is added to the solution before treatment with sodium. A like reaction occurs when an alcoholic solution of the disulphone is boiled with methyl iodide and alcoholic potash. Diethylsulphonedimethylmethane when treated in benzene solution with sodium does not evolve hydrogen. W. P. W.

Synthetical Experiments in the Sugar-group. By E. FISCHER and J. TAFEL (*Ber.*, **20**, 3384—3390; compare this vol., p. 39).—Glycerosazone (Abstr., 1887, 651) is prepared by adding 15 parts of bromine to a solution of 10 parts of glycerol and 35 parts of crystallised sodium carbonate in 60 parts of water at 10°. 200 grams of glycerol can be used in one operation. The solution is treated with 5 parts of phenylhydrazine hydrochloride. In five to eight days, the glycerosazone separates as a yellow, crystalline precipitate. The yield is 20 per cent. of the weight of glycerol.

When the oxidised glycerol is treated with aqueous soda, so that the amount of free alkali amounts to 1 per cent., and is kept for four to five days, the liquid loses the power of reducing alkaline copper solution in the cold; when warmed, it still has the power of reducing copper solutions. The solution is neutralised with acetic acid, and heated with phenylhydrazine hydrochloride and sodium acetate for six to eight hours. The product contains two osazones, $C_{18}H_{22}N_4O_4$. The one has all the properties previously ascribed to α -acrosazone (from acrylaldehyde bromide); it crystallises from alcohol in pure yellow, well-formed needles, which melt at 217° with decomposition. The other osazone is more readily soluble in ethyl acetate, from which it crystallises in globular groups of slender needles melting at 158—159°; it is probably identical with β -acrosazone. This method for preparing the acrosazones is more convenient than that previously described.

When a solution of 5 grams of dulcitol and 12 grams of sodium carbonate in 40 c.c. of water is treated with 5 grams of bromine, and the whole, half an hour afterwards, is warmed with 5 grams of phenylhydrazine and 5 grams of sodium acetate, the osazone, $C_{18}H_{22}N_4O_4$, separates in yellow flakes. This closely resembles galactosazone (Abstr., 1887, 562) except that it melts at 205—206° with decomposition. The name *phenyldulcitosazone* is ascribed to the new compound.

N. H. M.

Condensation of Formaldehyde. By O. LOEW (*Ber.*, **21**, 270—275).—The condensation of formaldehyde (Abstr., 1886, 609) is most readily effected by the action of strong bases, although it can be brought about by salts having an alkaline reaction, such as potassium sulphite or carbonate; salts having a neutral reaction are, however, without action on the aldehyde. Comparative experiments at 100° with aqueous solutions of lime and baryta containing equimolecular proportions of the two bases showed that the former rapidly acted on the aldehyde (15 per cent. solution) with the formation of formose as chief product, whilst the action of the latter resulted in the production of formic acid, much aldehyde remaining unaltered owing to the consequent neutralisation of the base. The production of formose by the action of lime-water is accelerated by the addition of sodium chloride, which itself does not bring about the condensation of the aldehyde, but is retarded by the presence of sodium acetate, potassium nitrate, and of much copper, iron, or tin. Calcined magnesia does not react with formaldehyde either in the cold or at 100°, but an aqueous solution of the hydroxide converts it into formose at 100°. Litharge and many lead salts also effect the condensation of the

aldehyde, and metallic lead acts in like manner; it is probable, however, that in this case the action is due to the presence of traces of the oxide, since the amount of the latter dissolved by shaking litharge with distilled water for some hours, adding 0.1 per cent. of the aldehyde, filtering and heating at 100° for two hours, sufficed to form formose. Iron, tetrethylammonium hydroxide, and many organic bases, also bring about the condensation.

When the osazone (m. p. = 123°) obtained from the sugar formed by heating a 0.5 per cent. solution of formaldehyde with tin for 15 hours (*ibid.*, 864) is heated in alcoholic solution at 100° for 25 to 30 hours, the melting point is found to have risen to 148° , at which it remains constant. A sugar, β -formose, which directly yields an osazone, $C_{18}H_{22}N_4O_3$, crystallising in small, yellow needles melting at 148° , is formed when a 0.1 per cent. solution of formaldehyde is heated for five hours with much tin. It is a thick, sweet, non-fermentable syrup, does not become brown at 100° , yields humous substances with hydrochloric acid, and its solution in alcoholic hydrogen chloride yields a wine-red colour with resorcinol, and a steel-blue colour with diphenylamine. 100 c.c. of Fehling's solution are reduced by 0.073 gram of the sugar.

If formaldehyde is added to an aqueous solution of magnesium hydroxide, prepared by treating a 5 to 10 per cent. solution of magnesium sulphate with litharge, until the mixture contains 0.3 per cent. of the aldehyde, and the whole is digested at 100° for many hours, a mixture of at least two non-fermentable sugars is obtained, one of which yields an osazone crystallising from benzene in yellow needles melting at 152° .

W. P. W.

Solubility of Calcium and Barium Formates, Acetates, and Propionates. By E. v. KRASNICKI (*Monatsh.*, 8, 595—606).—The solubilities of the different salts were determined by Raupenstrauch's method. The formulæ deduced from these determinations are given below:—

$$\text{Calcium formate, } S = 16.2978 + 0.03229(t - 0.8) - 0.0001254(t - 0.8)^2$$

$$\text{Barium formate, } S = 27.7744 + 0.0236743(t - 1) + 0.0063622(t - 1)^2 - 0.000060122(t - 1)^3$$

$$\text{Calcium acetate, } S = 37.8512 - 0.2575(t - 1) + 0.0058845(t - 1)^2 - 0.0000475576(t - 1)^3$$

$$\text{Barium acetate, } S = 58.473 + 0.65067(t - 0.8) - 0.005431(t - 0.8)^2$$

$$\text{Calcium propionate, } S = 41.2986 - 0.11196(t - 0.2) + 0.000085065(t - 0.2)^2 + 0.0000117907(t - 0.2)^3$$

$$\text{Barium propionate, } S = 48.2071 + 0.371205(t - 0.6) - 0.0015587(t - 0.6)^2.$$

The solubilities of the isobutyrate, isovalerate, and methylethylacetates, have been given by Sedlitzky (this vol., p. 250).

A. J. G.

Temperature of Conversion of Copper Calcium Acetate. By L. T. REICHER (*Zeit. physikal. Chem.*, **1**, 221—226).—That there is a temperature at which the crystals of this salt are converted into crystals of copper acetate and calcium acetate, is already rendered probable by the experiments of Kopp and Schuchardt. Microscopical examination confirms this supposition, for on heating the double salt up to about 80°, it separates into colourless needles of calcium acetate and green rhombic crystals of copper acetate. To determine the temperature of conversion exactly, a dilatometer was employed. The dilatometer was filled with the powdered double salt, exhausted and filled with mercury, and the change of volume at a given temperature was observed. It was found that the temperature of conversion lies between 78° and 76·2°.

C. S.

Preparation of β -Iodopropionic Acid. By V. MEYER (*Ber.*, **21**, 24—25).—The author describes in detail various modifications of the method previously given for the preparation of β -iodopropionic acid (*Abstr.*, 1887, 232).

F. S. K.

Analogy between Ketonic Acids and the Alkyl Sulphones of the Fatty Acids. By R. OTTO (*Ber.*, **21**, 89—99).—The larger portion of this paper deals with the points of analogy between the ketonic acids and the alkyl sulphones of the fatty acids.

β -Phenylsulphonepropionic acid, $\text{SO}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$, is prepared by neutralising β -iodopropionic acid and benzenesulphonic acid with sodium carbonate, and heating the product until no more water is given off. It forms shining, monosymmetrical or asymmetrical plates, is sparingly soluble in cold water, somewhat more soluble in ether, and melts at 123—124°. The alkali salts are described. The ethyl salt is a thick oil of a yellow colour, readily soluble in alcohol and ether, insoluble in water. The free acid is very stable; it does not react with the halogens, is not attacked by potash at 180°, but is totally decomposed at 280°; it is speedily reduced by sodium amalgam, the group PhSO_2 yielding a sulphinate.

J. W. L.

Isodibromosuccinic Acid. By R. DEMUTH and V. MEYER (*Ber.*, **21**, 264—270).—A repetition of Beilstein and Wiegand's experiments on isodibromosuccinic acid (*Abstr.*, 1882, 1051) shows that bromofumaric acid and not pyruvic acid is formed with the evolution of some carbonic anhydride when the barium salt is treated with moist silver oxide in the dark. Bromofumaric acid is also formed when the acid is heated with water for 10 hours in a reflux apparatus (Kekulé, *Annalen*, Suppl. **2**, 90), and racemic acid is obtained when the silver salt of the acid is boiled with water. Hence the unsymmetrical formula $\text{COOH}\cdot\text{CH}_2\cdot\text{CBr}_2\cdot\text{COOH}$ can no longer be ascribed to this acid. Attempts to prepare an acid of this formula by the oxidation of *aa*-dibromobutyric acid, $\text{EtCBr}_2\cdot\text{COOH}$, by displacing the oxygen of the carbonyl-group in acetoxalic acid by bromine, and by treating ethyl sodiomalonate with ethyl tribromacetate and saponifying the product led to no result, the crystalline compound formed

in the last experiment being free from bromine, whilst ethyl tricarbinetetracarboxylate, when treated with 1 mol. of bromine at 140° (compare Abstr., 1883, 46), yields a compound which on hydrolysis with concentrated hydrobromic acid yields carbonic anhydride and a crystalline compound free from bromine, and not symmetrical dibromosuccinic acid.

W. P. W.

Ethyl Oxalacetate. By W. WISLICENUS (*Ber.*, 20, 3392—3394; compare Abstr., 1887, 234).—Ethyl oxalacetate is prepared by shaking a solution of ethyl oxalate in four parts of ether with sodium ethoxide, previously freed from alcohol by heating in a current of hydrogen at 200°. The product is treated with ethyl acetate when the sodium compound separates; the yield is 70 per cent. of the theoretical. Ethyl oxalacetate boils at 131—132° under 24 mm. pressure, and reacts with ammonia and with aniline, yielding crystalline compounds. The *phenylhydrazine-derivative*, $C_{11}H_{13}N_2O_4$, crystallises in plates melting at 76—78°. When an alcoholic solution of the ethyl salt is treated with carbamide, the compound $C_9H_{14}N_2O_5 + EtOH$ separates in colourless crystals. The *hydroxylamine-derivative* is an oil. Nitrous acid reacts with ethyl oxalacetate in the cold, with formation of a crystalline isonitroso-derivative.

N. H. M.

Ethyl Methyloxalacetate. By W. WISLICENUS and E. ARNOLD (*Ber.*, 20, 3394—3396).—Ethyl methyloxalacetate, $C_9H_{13}O_5Na$, is prepared by the action of sodium ethoxide and ethyl propionate on ethyl oxalate dissolved in ether. It forms a colourless oil, boiling at 137—138° under 23 mm. pressure, insoluble in water, readily soluble in alcohol, ether, and alkali; the alcoholic solution gives an intense red coloration with ferric chloride. When boiled with alcoholic potash, it is converted into oxalic and propionic acids. Boiling dilute sulphuric acid decomposes it with formation of propionylformic acid (Claisen and Moritz, *Trans.*, 1880, 691). The *phenylhydrazine-derivative* of propionylformic acid, $CH_3Me \cdot C(N_2HPh) \cdot COOH$, crystallises from dilute alcohol in plates melting at 144—145°; when warmed with sulphuric acid and alcohol, and precipitated with water, *scatolecarboxylic acid*, $C_6H_4 < \begin{smallmatrix} CMe \\ NH \end{smallmatrix} > C \cdot COOH$, is obtained; this melts at 164—165°, decomposing into scatole and carbonic anhydride, and differs from Salkowski's compound (*Abstr.*, 1885, 568) in its crystalline form and in being more sparingly soluble.

N. H. M.

Cryoscopic Studies on Racemic Acids and Racemates. By F. M. RAOULT (*Zeit. physikal. Chem.* 1, 186—189).—In the case of solutions containing not more than 5 per cent. of acid, observation shows that equal quantities of dextrotartaric acid and racemic acid produce the same lowering of the freezing point, and it is inferred that the racemic acid is completely decomposed. For solutions of greater concentration, this will not be the case; part only will be decomposed. The fall of temperature produced by each unit of mass of this part will be known by observation. For the other, the fall caused by each

unit may be calculated from the law that the molecular fall of the freezing point is equal to 19 for all organic acids. The actual fall of temperature caused by the whole amount of racemic acid can be observed, and a simple equation will then give the amount of racemic acid decomposed. Thus it was found that out of 14.229 grams of racemic acid dissolved in 100 grams of water, 0.880 gram remained undecomposed.

In the case of the compounds, $C_4H_4O_6(NH_4)Na + 4H_2O$ and $2[C_4H_4O_6(NH_4)Na + H_2O]$, the fall of temperature is the same for solutions of the same strength up to about 13 per cent. C. S.

Organic Fluorine Compounds. By O. WALLACH and F. HEUSLER (*Annalen*, **243**, 219—244).—In the preparation of fluorobenzene (Abstr., 1887, 130), phenol and diphenyl ether, Ph_2O , are obtained as bye-products. Fluorobenzene can be obtained as a crystalline mass by exposure to the temperature produced by ether and solid carbonic anhydride. The index of refraction for Fraunhofer's line C is 1.4635; $\Delta_0 = 0.00017$. *Parafluoronitrobenzene* melts at 26.5° . *Parafluoranoliline* can be solidified by means of solid carbonic anhydride. The *acetyl*-derivative, $C_6H_4F \cdot NHAc$, melts at $150-151^\circ$. *Fluorobenzeneparadiazopiperidide*, $C_6H_4F \cdot N_2 \cdot C_5H_{10}$, is an unstable crystalline substance. *Paradifluorobenzene*, $C_6H_4F_2$, is liquid at the ordinary temperature. Its sp. gr. is about 1.11, and it boils between 37° and 89° .

Parafluorochlorobenzene, C_6H_4FCl , prepared from parafluoranoliline by means of Sandmeyer's method, boils at $130-131^\circ$. Its sp. gr. at 15° is 1.226. *Parafluorobromobenzene* melts between -15° and -20° , and boils at $152-153^\circ$. Sp. gr. 1.593 at 15° . *Parafluoriodobenzene* is prepared by the action of hydriodic acid on freshly prepared pure fluorobenzenediazopiperidide. It boils at $182-184^\circ$, and is decomposed by strong nitric acid, yielding iodine and fluornitrobenzene. *Parafluorophenol* boils at $186-188^\circ$.

Pseudocumenediazopiperidide, $C_6H_2Me_3 \cdot N_2 \cdot C_5NH_{10}$, is deposited from alcohol in thick prisms and melts at 50° . It is decomposed by hydrofluoric acid, yielding *fluoropseudocumene*, $C_6H_2Me_3F$, which melts at 27° and boils at $174-175^\circ$. *Chloropseudocumene* melts at $70-71^\circ$ and boils at $213-215^\circ$. The bromo-derivative melts at 72° and boils at $233-235^\circ$. *Iodopseudocumene* melts at 37° and boils at $256-258^\circ$. *Pseudocumenol* melts at 71° and boils at $234-235^\circ$. *Difluorodiphenyl*, $C_{12}H_8F_2$, is crystalline, and dissolves freely in alcohol and ether. It melts at $88-89^\circ$ and boils at $254-255^\circ$. Although Sandmeyer's method of converting amido-compounds into chloro- and bromo-substitution products yields admirable results, it is not to be recommended in the case of fluorides; the decomposition of diazoamido-compounds by hydrofluoric acid almost invariably yields better results in the latter case.

A comparison of the boiling points and specific gravity of the preceding compounds shows that (1) the substitution of hydrogen by fluorine increases the specific gravity, and has very slight influence on the boiling point; (2) the difference in boiling point between corresponding iodine and bromine substitution products, and between

bromine- and chlorine-derivatives is much smaller than the difference between chlorine and fluorine substitution products. The authors conclude that the boiling point of liquid fluorine is much lower than that of chlorine, and that it is probably near the boiling point of hydrogen.

Numerous experiments show that fluorine unites more firmly with carbon than chlorine, bromine, or iodine do. W. C. W.

Dichroïns. By H. BRUNNER and P. CHUIT (*Ber.*, **21**, 249—256).—Further experiments have confirmed the view put forward by Brunner and Krämer (*Abstr.*, 1884, 1354) that compounds analogous to Liebermann's colouring matters (this Journal, 1874, 693) are formed only from paranitrosophenol and those polyhydric phenols in which two hydroxyl-groups are in the meta-position relatively to one another. These compounds are now termed *dichroïns* from their fluorescent and dichroic properties, and are divided into two groups termed α - and β -dichroïns respectively. The α -dichroïns contain the group $C_6N(O\cdot C_6)_2$, and comprise the colouring matters, $C_{18}H_{15}NO_3$, derived from phenol (*Abstr.*, 1884, 1341), $C_{18}H_{15}NO_6$ and $C_{36}H_{26}N_2O_{10}$ from resorcinol (*Abstr.*, 1885, 525), and $C_{21}H_{21}NO_6$ from orcinol (*ibid.*); whilst the β -dichroïns contain the group $C_6N<\underset{O}{\underset{\curvearrowright}{O}}C_6$, and comprise the colouring matter, $C_{14}H_{11}NO_3$, derived from orcinol (*ibid.*), together with azoresorcinol, azoresorufin (*Abstr.*, 1884, 1333), and azoresorufyl ether, $C_{46}H_{50}N_2O_{13}$ (*Ber.*, **18**, 586), the last three compounds being termed β -resorcinol-, di- β -resorcinol-, and tetra- β -resorcinol-dichroïn respectively. In the majority of reactions by which dichroïns are formed, other colouring matters are also obtained differing from them in containing more oxygen and being destitute of fluorescence; these are termed oxychroïns.

Acetyl- α -phenoldichroïn, $OAc\cdot C_6H_4\cdot NO(OPh)_2$, prepared by heating α -phenoldichroïn (1 part) with acetic anhydride (3 parts) and anhydrous sodium acetate (2 parts) at 140° for an hour, is a brown, amorphous mass soluble in ether, alcohol, &c. *Acetylphenoloxychroïn*, $OAc\cdot C_6H_4\cdot N(OPh)_2$, was also prepared.

Orcinoldichroïn has the formula $C_6H_2(OH)_2Me\cdot N(O\cdot C_6H_3Me\cdot OH)_2$; its *acetyl*-derivative, $C_{21}H_{17}(OAc)_4NO_6$, is a brown, amorphous mass soluble in ether, alcohol, &c.

Thymoldichroïn was prepared by Liebermann's method (this Journal, 1875, 167), and when freed from unattacked thymol has the composition $O[N(C_6H_2MePr\cdot OH)_2]_2$. It sublimes at 140° with partial decomposition forming violet-coloured vapours, and is a dark-violet, amorphous mass, soluble in alcohol, ether, chloroform, and benzene yielding red solutions showing pale-green fluorescence. The *acetyl*-derivative, $C_{46}H_{48}(OAc)_4N_2O_5$, is a brown, amorphous mass, soluble in alcohol, ether, &c. In the purification of thymoldichroïn by steam distillation, thymoquinone passes over with the steam. Experiments show, however, that it is not a decomposition-product of thymoldichroïn, and to explain its formation the authors point out that nitrosothymol, unlike nitroso-phenol, -resorcinol, and -orcinol, seems to act as a quinoneoxime in the formation of its dichroïn, and regard it as probable

that in addition to this reaction a second also occurs in which a portion of the thymol reacts with thymoquinoneoxime to form amidothymol and thymoquinone (compare Sutkowski, Abstr., 1887, 41).

W. P. W.

Formation of Secondary Aromatic Amines. By A. PICTET (*Ber.*, **20**, 3422—3424).—Ethylacetanilide is prepared by adding 75 grams of finely-powdered acetanilide to a cold solution of 31 grams of caustic potash in 300 grams of 95 per cent. alcohol; after a short time the flask containing the mixture is fitted with a reflux condenser, 65 grams of ethyl bromide is added, and the whole slightly warmed on a water-bath. When the reaction becomes less violent, the mixture is heated for one to two hours, allowed to become cool, and filtered. The advantages of this method over Hepp's (*Ber.*, **10**, 327) are that it does not involve the use of large amounts of sodium, and that the product is more easily purified. The yield of ethylaniline (41 per cent. of the theoretical) is, however, not so good as that obtained by Hepp's method. In the case of formanilide, the yield is almost theoretical.

N. H. M.

Action of Sulphur on Dimethylaniline and Methylaniline. By R. MÖHLAU and C. W. KROHN (*Ber.*, **21**, 59—67).—When dimethylaniline is boiled with sulphur for 12 hours and distilled, an oil boiling at 210—345° is obtained. When this is treated with hydrochloric acid, it is separated into an oil of indifferent character which soon solidifies, and a mixture of several basic compounds. From the latter, Hofmann's methenylamidophenyl mercaptan (Abstr., 1887, 823, 1039), aniline, and methylaniline were separated. The indifferent crystalline substance has the formula $C_6H_7NS_2 \left(? N \begin{array}{c} \text{C}_6H_4-S \\ \text{CH}_2-S \end{array} CN \right)$, melts at 88—89°, and boils above 360°. When boiled with sulphur, it is converted into methenylamidophenyl mercaptan, and seems therefore to be the primary product. When treated with nitric acid, the compound $C_6H_7NS_2$ is changed into the base C_6H_7NS , probably $N \begin{array}{c} -CH_2- \\ \text{C}_6H_4-S \end{array} > CH$.

By the action of sulphur on methylaniline, the same compounds are obtained. The authors think that at first a decomposition of 2 mols. of methylaniline into dimethylaniline and aniline must have taken place, the dimethylaniline so formed then reacting with sulphur as described above.

J. W. L.

Action of Thiocarbonyl Chloride on Secondary Amines. By O. BILLETER and A. STROHL (*Ber.*, **21**, 102—110).—*Propylphenylthiocarbamine chloride*, $CSCl \cdot NPhPr$, crystallises from light petroleum in thick, colourless prisms melting at 36°. It is more stable in damp air than the corresponding methyl and ethyl compounds. *Dipropylthiocarbamilide*, $CS(NPhPr)_2$, forms colourless plates melting at 103.5°. *Methylpropylthiocarbamilide*, $NPhMe \cdot CS \cdot NPhPr$, prepared either from methyl chloride and propylaniline or from propyl chloride and methylaniline, forms colourless prisms melting at 56.5°.

Ethylpropylthiocarbamilide, $\text{NPhPr}\cdot\text{CS}\cdot\text{NPhEt}$, is prepared like the last-named compound and melts at $66\cdot3^\circ$. All these derivatives dissolve easily in concentrated acetic, hydrochloric, and sulphuric acids without change, whereas by warming with concentrated sulphuric acid or heating at 150° with hydrochloric acid the secondary base is readily eliminated.

Alcohols and phenols, the corresponding sulphur compounds, and also their metallic salts, react readily with the thiocarbamine chlorides already described, with formation of the corresponding thio- and dithio-carbamic acids. Of this series, the following were prepared:—*Ethyl ethylphenylthiocarbamate*, $\text{NEtPh}\cdot\text{CS}\cdot\text{OEt}$, prepared by the action of ethyl phenylcarbamine chloride on sodium ethoxide in ethereal solution, distils at $143\cdot6^\circ$ under a pressure of 12 mm. Sp. gr. 1.066 at 15° . It solidifies by prolonged cooling to a colourless, crystalline mass which melts at 18° . *Phenyl ethylphenylthiocarbamate*, $\text{NEtPh}\cdot\text{CS}\cdot\text{OPh}$, forms colourless needles and melts at $69\cdot2^\circ$. *Phenyl ethylphenyldithiocarbamate*, $\text{NPhEt}\cdot\text{CSSPh}$, crystallises in compact, colourless needles, and melts at $127\cdot8^\circ$. *Ethyl ethylphenyldithiocarbamate* melts at $66\cdot4^\circ$. A trisubstituted thiocarbamide is formed by the action of ethyl phenylthiocarbamine chloride, aniline, &c., and can be isolated by stopping the reaction after the mass first solidifies. It is decomposed if the reaction proceeds too far into thiocarbamilide and aniline hydrochloride. A small quantity of a dithiobiuret is also formed. The dithiobiurets are readily obtained by the further action of thiocarbamine chloride on the tertiary carbamides first formed.

Dimethyltriphenyldithiobiuret, $\text{C}_2\text{S}_2\text{N}_3\text{Ph}_3\text{Me}_2$, prepared from methylphenylthiocarbamine chloride and methylthiocarbamilide, forms yellow needles melting at $202\cdot5^\circ$. It is sparingly soluble in alcohol and ether, readily so in chloroform.

Diethyltriphenyldithiobiuret, $\text{C}_2\text{S}_2\text{N}_3\text{Ph}_3\text{Et}_2$, prepared from ethylphenylthiocarbamine chloride and ethylthiocarbamilide, crystallises in lemon-yellow needles melting at 158° . It is more readily soluble than the methyl compound.

Methylethyltriphenyldithiobiuret, (a), $\text{NEtPh}\cdot\text{C}(\text{NPh})\cdot\text{S}\cdot\text{CS}\cdot\text{NMePh}$, prepared from methylphenylcarbamine chloride and ethylthiocarbamilide, forms small, pale yellow needles melting at $157\cdot5^\circ$. It is soluble in chloroform, sparingly soluble in alcohol and ether. (b.) $\text{NMePh}\cdot\text{C}(\text{NPh})\cdot\text{S}\cdot\text{CS}\cdot\text{NEtPh}$, prepared from ethylphenylcarbamine chloride and methylthiocarbamilide, forms small, light-yellow needles like those of the (a) compound, and melts at $156\cdot5^\circ$.

Dipropyltriphenyldithiobiuret, $\text{C}_2\text{S}_2\text{N}_3\text{Pr}_2\text{Ph}_3$, prepared from propylphenylcarbamine chloride and propylthiocarbamilide, forms shining, yellow needles melting at $153\cdot7^\circ$. It is soluble in chloroform.

Methylpropyltriphenyldithiobiuret, $\text{C}_2\text{S}_2\text{N}_3\text{MePrPh}$ (a), prepared from methylphenylcarbamine chloride and propylthiocarbamilide, crystallises in shining yellow pyramids, melting point 110° ; (b) prepared from propylphenylcarbamine chloride and methylthiocarbamilide, forms yellow pyramids similar to the (a)-derivative, and melts at 111° .

Ethylpropyltriphenyldithiobiuret, $\text{C}_2\text{S}_2\text{N}_3\text{EtPrPh}_3$, (a) prepared from ethylphenylthiocarbamine chloride and propylthiocarbamilide, crystal-

lises in pale yellow needles melting at 165.8° . Very sparingly soluble in alcohol; (b) prepared from propylphenylthiocarbamine chloride and ethyl thiocarbamilide, crystallises in yellow needles melting at 165° .

Propylthiocarbamilide, $\text{CSN}_2\text{H}\cdot\text{Pr}\cdot\text{Ph}_2$, prepared from propylaniline and phenyl isothiocyanate, consists of colourless, shining needles which melt at 104.3° . It is readily soluble in alcohol, and is decomposed by hydrochloric acid into its components. J. W. L.

Constitution of Mixed Azo-compounds. By V. MEYER (*Ber.*, 21, 11—18).—The author had independently arrived at views on the constitution of the mixed azo-compounds identical with those brought forward by Japp and Klingemann (*Proc.*, 1887, 140).

Compounds of Phenylhydrazine with Ketone Alcohols. By H. LAUBMANN (*Annalen*, 243, 244—248).—*Benzoylcarbinolphenylhydrazone*, $\text{N}_2\text{HPh}:\text{CPh}\cdot\text{CH}_2\cdot\text{OH}$, crystallises in needles, melts at 112° , and dissolves freely in alcohol and ether. It is converted into an amorphous product, probably hydroxyphenylindole, by the action of zinc chloride at 150° . The hydrazone is converted into the osazone, $\text{N}_2\text{HPh}:\text{CPh}\cdot\text{CH}:\text{N}_2\text{HPh}$, by treatment with phenylhydrazine and sodium acetate in alcoholic solution. The osazone melts at 152° and is soluble in ether, benzene, and in hot alcohol.

The osazone of acetol is identical with the product v. Pechmann (*Abstr.*, 1887, 1103) obtained by the action of phenylhydrazine on nitrosoacetone. W. C. W.

Action of Phenylhydrazine on Dioximes. By M. POLONOWSKY (*Ber.*, 21, 182—184).—When glyoxime in alcoholic solution is treated with an equimolecular proportion of phenylhydrazine, an additive compound, $\langle \begin{smallmatrix} \text{CH}(\text{NOH}) \\ \text{CH}(\text{NOH}) \end{smallmatrix} \rangle \text{NH}_2\cdot\text{NHPh}$, is obtained. This crystallises from alcohol in white scales, melts at 110° , and is readily soluble in alcohol, less so in ether, and insoluble in water. Concentrated aqueous soda dissolves it, and the solution when heated yields phenylhydrazine; a like decomposition is also produced by concentrated sulphuric acid.

Under similar conditions diphenylglyoxime yields an additive compound, $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_2$, which crystallises in needles, melts at 149 — 150° , and closely resembles the preceding derivative in its properties.

β -Naphthaquinonedioxime, in like manner, forms an additive compound, $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_2$. This crystallises from alcohol in tufts of long needles, begins to fuse at 105° , and melts at 138° . W. P. W.

Aldines and Amidoacetophenone. By E. BRAUN and V. MEYER (*Ber.*, 21, 19—21).—When isonitrosoacetophenone is reduced in hydrochloric acid solution, it is completely transformed into the hydrochloride of an amidoacetophenone, $\text{COPh}\cdot\text{CH}_2\cdot\text{NH}_2$. This salt crystallises from water in large, hard, colourless crystals, and is very stable; it can be recrystallised from hot water, and forms a crystalline platinumchloride. The freshly precipitated base redissolves in acids,

but when purified by washing or recrystallising from alcohol, it becomes orange-coloured, and completely loses its basic properties, being converted into a coloured crystalline substance, which resembles isoindole very closely, and with which it is probably identical. A ketine, $N \begin{smallmatrix} \diagup \text{CPh} : \text{CPh} \\ \diagdown \end{smallmatrix} N$, is readily obtained from the monoxime of benzil.

F. S. K.

Formation of Phenylhydrazide Acids from the Anhydrides of Bibasic Acids. By R. ANSCHÜTZ (*Ber.*, **21**, 88—89).—By the action of phenylhydrazine on the chloroform or ethereal solutions of the bibasic anhydrides, the corresponding phenylhydrazide acids are obtained. The following anhydrides react in this way: maleïc, succinic, citraconic, itaconic, camphoric, phthalic, diphenylmaleïc, phthalic, diphenylmaleïc, and diphenylsuccinic (compare Hötte, *Abstr.*, 1887, 669).

J. W. L.

Formation of Orthosulphaminecarboxylic Acids. By C. FAHLBERG and R. LIST (*Ber.*, **21**, 242—248).—The products of the oxidation of orthotoluenesulphonamide under different conditions were examined, and the results show that when the oxidation is carried on in alkaline solutions by potassium ferricyanide (*Abstr.*, 1886, 804), by potassium manganate, and by potassium permanganate, orthosulphaminebenzoic acid is formed; that when it is carried on in neutral solutions by permanganate, benzoic sulphinide is the chief product, a small quantity of orthosulphaminebenzoic acid being also formed, probably by the action of the alkali produced by the decomposition of the permanganate, since the yield was much diminished by adding acid from time to time to neutralise the alkali formed; and that when it is carried on by permanganate in solutions rendered acid either by hydrochloric acid, or by a current of carbonic anhydride, orthosulphobenzonic acid and potassium nitrate are formed. Benzoic sulphinide is to be regarded as the primary product of the oxidation, since on evaporation with hydrochloric acid it is converted into orthosulphobenzonic acid and ammonia, and on evaporation with potassium hydroxide into orthosulphaminebenzoic acid. Ammonia, alkaline carbonates, and the oxides of the alkaline earths cannot be employed for this purpose; moreover, in the case of barium oxide, the barium salt of the sulphinide is obtained (compare this vol., p. 282).

Orthoparadisulphaminebenzoic acid, $[\text{COOH} : \text{SO}_2\text{NH}_2 : \text{SO}_2\text{NH}_2 = 1 : 2 : 4]$, is obtained either by oxidising orthoparatoluenedisulphonamide with alkaline potassium manganate, or by evaporating sulphaminebenzoic sulphinide with potassium hydroxide. It crystallises in slender, satiny, microscopic needles, melts at 182—183°, is completely decomposed at 250—260°, and is very soluble in water and alcohol, sparingly soluble in ether. The salts of the alkalis and alkaline earths are readily soluble, and those of the metals are sparingly soluble in water. The *barium* salt, with 5 mols. H_2O , crystallises in large, colourless, monoclinic prisms, the *copper* salt, with 2 mols. H_2O , in bright-blue, silky needles, and the *silver* salt in anhydrous, white needles. The *ethyl* salt is identical with that pre-

pared from disulphaminebenzoic acid (Abstr., 1881, 816). For purposes of comparison, the corresponding salts of disulphaminebenzoic sulphinide were prepared; the *barium* salt, with $3\frac{1}{2}$ mols. H_2O , crystallises in granular aggregates of needles, and the *copper* salt, with 4 mols. H_2O , in blue, microscopic needles; the *silver* salt is anhydrous and indistinctly crystalline.

W. P. W.

Derivatives of Phenyldibromisobutyric Acid. By A. KÖRNER (*Ber.*, 21, 276—277).—When α -methylcinnamic acid (m. p. = 78°) dissolved in carbon bisulphide is treated with bromine, *phenyldibromisobutyric acid*, $CHPhBr \cdot CMeBr \cdot COOH$, melting at 137° , is obtained. This, when warmed with alcoholic potash, yields *bromophenylcrotonic acid*, $CPhBr : CMe \cdot COOH$, which crystallises from water in matted needles, and melts at 124° . If phenyldibromisobutyric acid is boiled with water, *phenylbromohydroxyisobutyric acid* is formed, melting at 148° . In both cases, the yield of the acid is small, the chief product being *phenylbromopropylene*, C_6H_5Br ; this is a colourless liquid, of pleasant odour, and boils at 226° with decomposition. When treated with alcoholic potash, it is converted into *phenylallylene*, $CPh : CMe$; this is a pale-yellow liquid of unpleasant odour, boils at 185° , and yields with bromine a liquid *dibromide*, which boils at 250 — 255° with the evolution of much hydrogen bromide, and a solid *tetrabromide*, which crystallises in lustrous plates and melts at 75° . On treatment with an aqueous solution of mercuric chloride, phenylallylene forms a white, amorphous compound,



which when heated with hydrochloric acid yields not phenylallylene but phenyl ethyl ketone, $COEtPh$.

W. P. W.

Parisobutylorthohydroxybenzoic Acid. By L. v. DOBRZYCKI (*J. pr. Chem.* [2], 36, 389—400).—Anhydrous sodium isobutylphenoxide was prepared by adding the exactly equivalent quantity of isobutylphenol (Liebmann, Abstr., 1882, 171) to alcoholic sodium ethoxide, evaporating off the alcohol, and drying the phenoxide at 140 — 150° in a stream of hydrogen. The dry phenoxide was then treated, under pressure, with carbonic anhydride, which was rapidly absorbed with evolution of much heat, sodium isobutylphenyl carbonate being formed. When this substance was heated for some time at 130 — 160° it yielded *sodium parisobutylorthohydroxybenzoate*. The free acid, $C_6H_5 \cdot C_6H_3(OH) \cdot COOH$, is soluble in boiling water, volatile in steam, and crystallises in long, thin, glistening, white needles. It dissolves readily in alcohol, ether, and chloroform. The aqueous solution gives an intense violet coloration with ferric chloride. The metallic salts are not well characterised. The *methyl* salt yields large, colourless prisms, melts at 54° , and boils at 266° . It is easily soluble in alcohol and ether. Cold soda converts it into a white mass probably of the formula $C_6H_5 \cdot C_6H_3(ONa) \cdot COOMe$. The *ethyl* salt is a colourless aromatic liquid boiling at 276° . The *phenyl* salt was prepared by heating the acid with phenol at 130° , and adding the requisite quantity of phosphoric chloride in small quantities. It forms

long, glistening needles, sparingly soluble in cold ethyl and methyl alcohols, easily in ether, and melts at 68°. Dilute soda does not attack it in the cold, but saponifies it on heating. When heated in a reflux apparatus, carbonic anhydride is evolved, and phenol, isobutylphenol, and *isobutylbenzophenoxide*, $C_{17}H_{16}O_2$, are formed. The latter compound is now being investigated.

When isobutylphenol is treated with phosphoric chloride, *isobutylchlorobenzene* is formed. The oxidation of this compound proved difficult, potassium chromate and sulphuric acid solution being without action, whilst chromic acid in acetic solution caused complete oxidation. When heated for a long time at 190° with dilute nitric acid, however, it yielded parachlorobenzoic acid. Liebmann's isobutylphenol is, therefore, the para-compound, and from analogy and a consideration of its properties there is little doubt that the acid described above has the constitution $[OH : COOH : C_4H_9 = 1 : 2 : 4]$.
L. T. T.

α -Methylcinnamic Acid. By P. RAIKOW (*Ber.*, 20, 3396—3397).—In preparing α -methylcinnamic acid (phenylcrotonic acid) by Perkin's method, and recrystallising the product from light petroleum, two acids were obtained having the same composition. The one crystallises in plates melting at 81—82°, the other in needles melting at 74°. When the latter is often recrystallised, it is converted into the acid of higher melting point. The relative amounts of the two acids is influenced by the temperature at which the reaction between the benzaldehyde, propionic acid, and sodium acetate takes place. At 135°, 24 per cent. of the plates and 30 per cent. of the needles are obtained, whilst at 175° only the needles (56 per cent.) are formed. The two acids differ only slightly in solubility.
N. H. M.

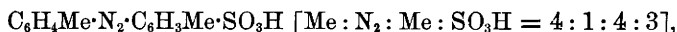
Benzeneazomalonic Acid. By R. MEYER (*Ber.*, 21, 118—119).—Benzeneazomalonic acid, prepared from diazobenzene chloride and ethyl malonate, is identical with the phenylhydrazide of mesoxalic acid.
J. W. L.

Action of Phthalic Anhydride on Amido-acids. By L. REESE (*Ber.*, 21, 277—278).— α -Leucinphthalic acid (this vol., p. 148) can be obtained by adding the calculated quantity of phthalyl chloride to a boiling solution of leucine in alcoholic potash, and continuing the boiling of the alkaline solution for one minute; on cooling, the potassium salt crystallises in small, slender, concentrically-grouped needles, and yields the acid on treatment with dilute sulphuric acid and extraction with ether.

Phthalylidisarcosine, $C_{14}H_{16}N_2O_6$, is formed when phthalic anhydride (5 parts) is heated at 140—150° with sarcosine (6 parts). It crystallises in lustrous needles, melts at 168°, and is readily soluble in water and boiling alcohol, sparingly soluble in ether, and insoluble in chloroform and light petroleum. A sodium salt could not be prepared, since the compound is decomposed into its constituents by the action of alkalis; a similar decomposition also occurs when it is heated with concentrated hydrochloric acid.
W. P. W.

Azotoluenesulphonic Acid. By J. V. JANOVSKY (*Ber.*, **21**, 119—122).—By appropriate manipulation, it is possible to directly sulphonate azotoluene.

Azotoluenesulphonic acid,



is obtained by the action of fuming sulphuric acid on paratzotoluene, care being taken that the temperature is kept below 100° ; the best result is obtained by the employment of an acid containing about 24 per cent. SO_3 , when the temperature produced by the reaction does not exceed 80° . It crystallises with 5 mols. H_2O in orange-red tables, sparingly soluble in cold water. The potassium (with 5 mols. H_2O), sodium ($4\frac{1}{2}$ mols. H_2O), calcium, barium (11 mols. H_2O), lead and zinc salts are described. When nitrated, it yields a *nitro-acid*, $\text{NO}_2\cdot\text{C}_{14}\text{H}_{12}\text{N}_2\cdot\text{SO}_3\text{H} + \text{H}_2\text{O}$, crystallising in small, yellow needles, readily soluble in hot water; several salts were prepared. The corresponding *amido-acid* crystallises in pale-yellow needles, and together with the *hydrazo-acid* also obtained, will be described later. A *bromo-acid*, $\text{C}_{14}\text{H}_{12}\text{BrN}_2\cdot\text{SO}_3\text{H}$, was prepared, crystallising in tufts of long needles; the potassium and calcium salts are described. Proof of the constitution assigned above to the sulphonic acid is obtained when it is treated with tin and hydrochloric acid, paratoluidine hydrochloride, and paratoluidineorthosulphonic acid [$\text{Me} : \text{SO}_3\text{H} : \text{NH}_2 = 1 : 2 : 4$] being formed.

A. J. G.

Ethylindole. By A. PICTET and L. DUPARC (*Ber.*, **20**, 3415—3422).—*3'-Ethylindole* is prepared as follows:—30 grams of aniline is added to 50 grams of zinc chloride, and the whole mixed with 35 grams of lactic acid; 200 to 300 grams of sand being added to prevent frothing. It is then heated in a copper retort. The oily products of several fractions are united, dissolved in ether and shaken with small amounts of dilute hydrochloric acid until no more basic substance is dissolved; the ethereal solution is then distilled. It is a bright yellow oil, boiling at $282\text{--}284^\circ$ (corr.), very sparingly soluble in water, readily soluble in alcohol, ether, benzene, and chloroform, &c.; it distils readily with steam. When the alcoholic solution is treated with hydrochloric acid and a chip of pine, it gives an intense red colour. The solution in chloroform gives, on addition of a few drops of a dilute solution of bromine in chloroform, an intense violet coloration, resembling that of potassium permanganate. The picrate melts at 143° . Ethylindole resembles scatole in its general behaviour.

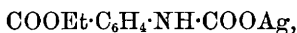
The basic substance formed in the preparation of ethylindole is quinaldine (compare Wallach and Wüsten, *Ber.*, **16**, 2067).

Propionylorthotoluidine, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{COEt}$ [$\text{Me} : \text{NH}\cdot\text{COEt} = 1 : 2$], is readily obtained by boiling orthotoluidine with propionic acid for six hours. It crystallises from benzene in white needles an inch long, melts at 87° , and is readily soluble in alcohol, ether, and glacial acetic acid, &c., sparingly soluble in hot water. It boils at $298\text{--}299^\circ$ (corr.) under 730 mm. pressure. When oxidised with potassium permanganate, it is converted into *propionylorthamidobenzoic acid*, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{COEt}$. This crystallises from water in white, flat

needles, melts at 117° , decomposes at 180° and is readily soluble in alcohol, ether, and in hot water. The *silver salt* crystallises from water in small, white needles. N. H. M.

Dimethylindole. By L. WOLFF (*Ber.*, **21**, 123—126).—Aniline reacts with β -bromolævulinic acid, forming dimethylindole, $C_{10}H_{11}N$. The vapour-density shows that this is the product of the reaction and not a compound of twice this molecular formula, as the author suggested in a former paper (*Abstr.*, 1887, 464—465). This indole is identical in all respects with the 2'.3' dimethylindole obtained by E. Fischer (*Abstr.*, 1887, 149). J. W. L.

Isatoic Acid. By G. SCHMIDT and E. v. MEYER (*J. pr. Chem.*, [2], **36**, 370—389).—When isatoic acid is heated in closed tubes at 100° with excess of ethyl alcohol, *hydrogen ethyl carboxylanthranilate*, $COOEt \cdot C_6H_4 \cdot NH \cdot COOH$, is formed. It crystallises in thin, colourless needles, melts at 126° , and is soluble in boiling water. When heated with hydrochloric acid in closed tubes at 150° this substance yields carbonic anhydride, ethyl chloride and anthranilic acid hydrochloride. The salts of this acid are crystalline; the *silver salt*,



forms white, microscopic needles or prisms, which are soluble in alcohol and sensitive to light.

When methyl alcohol is substituted for ethyl alcohol in the above reaction *hydrogen methyl carboxyanthranilate*, $COOMe \cdot C_6H_4 \cdot NH \cdot COOH$, is formed. This crystallises in minute needles, soluble in boiling water and melting at 176° . The *silver salt* forms small needles which are less stable than the ethyl compound. When heated with hydrochloric acid at 120° , the methyl compound dissolves, but on cooling crystallises out again unchanged. When heated at 200° with an indifferent substance, such as glycerol, carbonic anhydride is evolved, and methyl anthranilate is formed.

With phenol at 180° , isatoic acid yields *phenyl anthranilate*, $NH_2 \cdot C_6H_4 \cdot COOPh$, but no carboxyl-derivative. The phenyl salt crystallises in colourless needles melting at 70° . It is easily soluble in alcohol and in ether, sparingly so in boiling water. It is slightly volatile in a current of steam.

When warmed with freshly precipitated ferrous hydrate in the presence of excess of soda, isatoic acid is reduced to anthranilic acid. With zinc-dust and acetic acid, isatoic acid yields anthranilcarboxylic acid, $\langle \overset{CO-}{C_6H_4} \rangle N \cdot COOH$.

When isatoic acid is heated with glacial acetic acid, carbonic anhydride is evolved, and a compound of the formula $C_{36}H_{27}N_5O_8$ formed. This substance is almost insoluble in the usual solvents, and only melts at a very high temperature. At 150° , it is soluble in ammonia, but crystallises out again unchanged on cooling. With hydrochloric acid at 190° , it yields anthranilic acid hydrochloride. It dissolves in cold concentrated sulphuric acid with slight darkening, but is reprecipitated unchanged on the addition of water. 50 per

cent. sulphuric acid at 160° converts it into anthranilic acid. The compound is probably formed from 5 mols. of isatoic acid by the separation of 4 mols. of water. If acetic anhydride is used in place of acetic acid, carbonic anhydride is evolved, and acetylanthranilic acid is formed.

Meyer has already pointed out (Abstr., 1885, 666) that anthranilcarboxylic acid is formed from isatoic acid by oxidising as well as by reducing agents.

From a careful consideration of all the experimental results obtained, the authors conclude that isatoic acid is really identical and not isomeric with anthranilcarboxylic acid, and that the seeming differences of properties are due to the presence in isatoic acid of small quantities of a yellow-coloured impurity. This impurity, which modifies the properties of the acid, is not removed by the ordinary methods of purification, but is destroyed by strong oxidising or reducing agents.

Finally, the authors are inclined to think that the ethyl-compound described above is perhaps identical with that obtained by Weddige by the action of ethyl chlorocarbonate on anthranilic acid, in which case its constitution would be $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{COOEt}$, and that of the methyl-compound analogous to it.

L. T. T.

Action of Glyoxal on Aromatic Amines. By O. HINSBERG (*Ber.*, 21, 110—118).—It is easy to obtain reactions between aromatic monamines and glyoxal, if, instead of employing the latter in the free state, its compound with sodium hydrogen sulphite is used.

Anilidoacetanilide, $\text{NHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, is prepared by heating aniline and glyoxal sodium hydrogen sulphite with dilute alcohol in the water-bath for 20 to 30 hours. The melting point, 112—113°, is found to be rather higher than has previously been stated. Under like conditions, paratoluidine gives paratoluidoacetotoluide.

When β -naphthylamine is heated with glyoxal sodium hydrogen sulphite in alcoholic solution, the reaction takes another course and the sodium salt of β -naphthoxindolesulphonic acid separates. The free acid could not be obtained. The potassium salt, $\text{C}_{12}\text{H}_9\text{N}\cdot\text{SO}_3\text{K}$, crystallises in white plates, and when heated with aqueous hydrochloric or sulphuric acid at 80—90° yields β -naphthoxindole whilst much sulphurous anhydride is evolved.

β -Naphthoxindole, $\text{C}_{10}\text{H}_6\langle\begin{smallmatrix} \text{NH} \\ \text{CH}_2 \end{smallmatrix}\rangle\text{CO}$, crystallises in pale green needles, melts at 234°, and is sparingly soluble in water, readily in alcohol, ether, and glacial acetic acid. It dissolves in potash without decomposition, and is insoluble in mineral acids, but with concentrated sulphuric acid it gives a bluish-green coloration which disappears on dilution. The isonitroso-compound, $\text{C}_{10}\text{H}_6\langle\begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{C}(\text{NOH}) \end{smallmatrix}\rangle$, prepared by the action of nitrous acid, forms slender, reddish-yellow needles, and melts at 240°.

β -Naphthhisatin, $\text{C}_{10}\text{H}_6\langle\begin{smallmatrix} \text{NH} \\ \text{CO} \end{smallmatrix}\rangle\text{CO}$, is prepared by reducing isonitroso- β -naphthoxindole in dilute alcoholic solution by zinc and

hydrochloric acid, and treating the colourless liquid so obtained with ferric chloride. It forms slender, red needles, melts at 248° , is moderately soluble in the ordinary solvents, and resembles isatin in its chemical behaviour.

From α -naphthylamine, the corresponding α -compounds were obtained in similar manner. The sodium and silver salts of α -naphth-indolesulphonic acid were prepared, but the free acid could not be obtained.

α -Naphthoxindole crystallises in colourless needles, melts at 245° , is insoluble in aqueous soda, and gives a greenish-black coloration with ferric chloride and hydrochloric acid. The isonitroso-compound forms yellowish-red needles, sinters, and turns black at 230° , and is completely fused at 260° .

α -Naphthisatin forms red needles, melts at 255° ; the phenyl-hydrazide melts at 268 – 270° . Neither of the naphthisatins give the blue coloration with sulphuric acid and benzene containing thiophen.

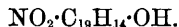
A. J. G.

Condensation-compounds of Metanitrobenzaldehyde with Benzene and Toluene. By O. TSCHACHER (*Ber.*, 21, 188–191).—Metanitrotriphenylmethane, $\text{CHPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, is formed when a solution of metanitrobenzaldehyde in benzene is shaken with half its volume of sulphuric acid; it crystallises from light petroleum in colourless crystals, and melts at 90° . When reduced in acetic acid solution with zinc-dust, it yields the *amido*-derivative, which crystallises from ether in short needles, melts at 120° , and forms a *hydrochloride*,



The *acetyl*-derivative, $\text{C}_{19}\text{H}_{15}\cdot\text{NHAc}$ crystallises in colourless, nacreous scales, melts at 115° , and is soluble in alcohol.

When metanitrotriphenylmethane in carbon bisulphide solution is treated with the calculated quantity of bromine and exposed to sunlight, an oil, probably $\text{C}_{19}\text{H}_{14}\cdot\text{Br}\cdot\text{NO}_2$, is obtained which on treatment with potassium acetate in acetic acid solution, and subsequent hydrolysis with aqueous potash, yields *metanitrotriphenyl carbinol*,



This crystallises from light petroleum in colourless crystals, and melts at 75° ; when reduced, it is converted into the *amido*-derivative, which crystallises from ether in colourless, stellate forms, melts at 155° , and yields an *acetyl*-derivative, $\text{OH}\cdot\text{C}_{19}\text{H}_{14}\cdot\text{NHAc}$, crystallising in colourless, nacreous scales and melting at 164° .

Metanitrophenylditolylmethane, $\text{CH}(\text{C}_6\text{H}_4\text{Me})_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, is obtained by treating a solution of metanitrobenzaldehyde in toluene with sulphuric acid in the cold. It crystallises from light petroleum in colourless forms, and melts at 85° .

W. P. W.

Action of Dichlorether on Phenol. By J. WISLICENUS and H. REINHARDT (*Annalen*, 243, 151–165).—Dichlorether acts on phenol,

forming *ethenyltriphenol*, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}\cdot(\text{C}_6\text{H}_4\cdot\text{OH})_2$, and other products. If less than 3 mols. of phenol are taken, an insoluble resin is formed. The crude product is dissolved in alkali, reprecipitated by hydrochloric acid, and distilled in a current of steam to remove the excess of phenol. These three operations must be repeated several times. Ethenyltriphenol yields a triacetate soluble in ether, alcohol, chloroform, acetone, benzene, aniline, phenol, and acetic acid. The acetic acid solution is oxidised by ferric chloride, yielding *isorosolic acid*, $\text{C}_{20}\text{H}_{16}\text{O}_8$, a dark, carmine-red, amorphous powder. Isorosolic acid yields a sulphonic acid. From an acetic acid solution of isorosolic acid, chromic acid throws down an amorphous insoluble compound containing chromium.

W. C. W.

Action of Dichlorether on the Dihydroxybenzenes. By J. WISLICENUS and M. SIEGFRIED (*Annalen*, **243**, 171—192).—*Ethenyltri-resorcinol*, $\text{C}_2\text{H}_3[\text{C}_6\text{H}_3(\text{OH})_2]_3$, is formed by the action of dichlorether (14 grams) on 33 grams of resorcinol dissolved in 300 grams of benzene. It is a pale-red, amorphous powder soluble in water, alkalis, alcohol, acetone, and in strong acetic acid. It is precipitated by hydrochloric acid from alkaline solutions, and after the precipitate has been dried in a vacuum, it is sparingly soluble in water, alcohol, and acetic acid. A monacetic derivative is obtained by the action of glacial acetic acid at 85° . It is insoluble in the ordinary solvents, and is converted into an insoluble hexacetate by the action of acetic anhydride at 200° . By the action of acetic anhydride on ethenyltri-resorcinol at 170° , an amorphous hexacetate is obtained which is soluble in acetone, chloroform, benzene, and acetic acid. A chocolate-coloured, amorphous substance is formed by boiling ethenyltri-resorcinol with glacial acetic acid and ferric chloride. When freshly prepared, it is soluble in alcohol, acetone, and acetic acid. It also dissolves in alkalis, yielding a cherry-red solution. It yields a pentacetate, $\text{C}_{20}\text{H}_{11}(\text{Ac})_5\text{O}_6$. When bromine acts on ethenyltri-resorcinol, two hydrogen-atoms are eliminated and six are substituted by bromine, yielding $\text{C}_{20}\text{H}_9\text{Br}_6\text{O}_6$, a substance soluble in alcohol, ether, acetone, chloroform and acetic acid.

Ethenyltricatechol is obtained as an amorphous compound by the action of dichlorether on a mixture of pyrocatechol and benzene. It is soluble in alcohol, acetone, acetic acid, and alkalis. It yields a hexacetate. On oxidation with ferric chloride, it loses two atoms of hydrogen, but the product could not be obtained in a pure state, although its pentacetate, $\text{C}_{20}\text{H}_{11}(\text{Ac})_5\text{O}_6$, was prepared. Bromine converts ethenyltricatechol into the hexabromide, $\text{C}_{20}\text{H}_9\text{Br}_6\text{O}_6$, from which the pentacetate, $\text{C}_{20}\text{H}_9\text{Br}_6\text{Ac}_5\text{O}_6$, was obtained.

Ethenyltri-quinol is prepared by the action of dichlorether on a solution of quinol in warm ethyl acetate. It is an amorphous substance, soluble in alcohol, acetone, acetic acid, and in alkalis. The hexacetate is soluble in acetone, chloroform, and acetic acid. Ethenyltri-quinol yields a green colouring matter, $\text{C}_{20}\text{H}_{16}\text{O}_6$, when it is treated with ferric chloride; a bromide, $\text{C}_{20}\text{H}_7\text{Br}_6\text{O}_6$, can also be prepared. When an excess of dichlorether acts on a solution of quinol in ethyl acetate,

a resin and a soluble compound are formed. The latter resembles ethenyltriquinol, but has the composition $C_{16}H_{13}ClO_4$.

W. C. W.

Action of Sulphur on the Salts of Aromatic Hydroxy-compounds. By M. LANGE (*Ber.*, **21**, 260—264).—When β -naphthol is dissolved in aqueous soda and boiled with an excess of sulphur, the latter dissolves and *dihydroxydinaphthyl disulphide*, $S_2(C_{10}H_6\cdot OH)_2$, is formed. This crystallises in white, opaque needles, melts at 210° (uncorr.) and is insoluble in water, sparingly soluble in ethyl alcohol, readily soluble in acetic acid, benzene, amyl alcohol, alkalis, and alkaline sulphides. From the mother-liquors, a second compound of like composition can be separated, which crystallises in long, yellow needles, melts at 168 — 170° , is more soluble in all solvents than dihydroxydinaphthyl disulphide, and is also distinguished from it by its greater acidity. Both compounds yield β -naphthol on distillation and when heated with alkalis or ammonia at 150° . Dihydroxydinaphthyl disulphide is alone formed when β -naphthol is heated with sulphur and lead oxide at 180 — 200° .

Resorcinol, when treated in like manner, yields a compound, $C_6H_4O_2S_2$, provisionally termed thioresorcinol. It is a yellow powder, which carbonises before fusion, and is almost insoluble in the ordinary solvents, but readily soluble in alkalis, alkaline carbonates, and alkaline sulphides.

W. P. W.

Action of Fuming Sulphuric Acid on α -Naphthylamine Hydrochloride. By R. MAUZELIUS (*Ber.*, **20**, 3401—3404).—The sulphonic acid prepared by Witt (*Abstr.*, 1886, 554), by the action of fuming sulphuric acid on α -naphthylamine hydrochloride, is shown to be α -amidonaphthalenesulphonic acid. The acid was prepared exactly as described by Witt (*loc. cit.*), and was purified by means of the calcium salt. The different results obtained by Witt appear to be due to the presence of some impurity.

N. H. M.

α -Naphthaldehyde. By E. BAMBERGER and W. LODTER (*Ber.*, **21**, 256—260).—When equimolecular proportions of α -naphthabenzylamine hydrochloride and sodium nitrite are dissolved in water, the *nitrite* of the base, $C_{10}H_7\cdot CH_2\cdot NH_2\cdot HNO_2$, is obtained; this crystallises from water, in which it is sparingly soluble, in long, slender prisms, and melts and suddenly decomposes at 148.5° .

α -Naphthabenzyl alcohol, $C_{10}H_7\cdot CH_2\cdot OH$, is prepared by diazotising the amine. It crystallises in long, lustrous needles, melts at 59 — 60° , boils at 301° (corr.) under 715 mm. pressure, and is readily soluble in alcohol and ether, less soluble in hot water. On oxidation with potassium dichromate and sulphuric acid, it is converted into α -naphthaldehyde, $C_{10}H_7\cdot CHO$. This is a thick, pale-yellow oil of slightly aromatic odour, which boils at 291.6° (corr.) without decomposition and gives the characteristic aldehyde reactions; the *phenylhydrazide* crystallises in lustrous, bright-yellow scales and melts at 185° . On treatment with nitric acid (sp. gr. = 1.47) at -5 — 0° , a mixture of nitraldehydes is obtained, one of which crystallises in lustrous, pale-yellow needles, melts at 136° , is very sparingly soluble in cold alcohol

and does not give a colour reaction with acetone and aqueous soda. α -Naphthaldehyde could not be obtained by distilling calcium α -naphthoate with calcium formate. W. P. W.

1 : 4' Bromonaphthalenesulphonic Acid. By R. MAUZELIUS (*Ber.*, **20**, 3404—3407).—1 : 4' Bromonaphthalenesulphonic acid (Darmstädter and Wichelhaus, *Annalen*, **152**, 303) is prepared by adding 1 : 4' diazonaphthalenesulphonic acid to warm, strong hydrobromic acid; the solution is neutralised with potassium carbonate, the potassium salt recrystallised from hot water, dried and rubbed with phosphorus pentachloride; the product is then treated with water, extracted with ether, and crystallised from glacial acetic acid. The chloride is heated with water at 130°. The impure acid melts at 126°. The *barium salt* (with 2 mols. H_2O) is sparingly soluble; the *silver salt* crystallises in pale-yellow lustrous scales. The chloride crystallises in well-formed crystals melting at 94°. The amide forms yellowish needles melting at 232—233°. The *ethyl salt* crystallises well, dissolves readily in alcohol, chloroform, and ether, &c., and melts at 51° (compare also Jolin, *Verhand. d. schwed. Akad. d. Wissensch.*, 1877, No. 7). N. H. M.

Reduction of the Thiamides of Aromatic Acids. By E. BAMBERGER and W. LODTER (*Ber.*, **21**, 51—56).—When an aromatic thiamide is reduced with zinc and hydrochloric acid, a benzylamine base is not the only product, a hydrocarbon is obtained at the same time in quantities of about 1 to 2 per cent. of the thiamide employed.

Symmetrical *di- α -naphthylethane*, $C_{10}H_7 \cdot CH_2 \cdot CH_2 \cdot C_{10}H_7$, is formed in the reduction of α -naphthothiamide in alcoholic solution; on evaporation, an oily resinous mass is obtained; this is treated with soda, and the oil which separates is distilled. As soon as the naphthobenzylamine has passed over, the thermometer rises rapidly above 360° and a thick yellow oil distils, and in a short time solidifies. The dinaphthylethane thus obtained, after purification and crystallisation from alcoholic benzene, forms shining, hexagonal plates which are readily soluble in benzene and chloroform, less so in ether, and sparingly soluble in alcohol with a green fluorescence. The crystals are greenish-yellow, and melt at 160° to a yellow oil with moss-green fluorescence.

Symmetrical *di- β -naphthylethane* is obtained by extracting with benzene the resinous product formed in the reduction of β -naphthothiamide. It crystallises from benzene and chloroform in shining silver-white, plates melting at 253°, is only sparingly soluble in ordinary solvents, most readily in chloroform and benzene, and less so in boiling alcohol and ether; the solutions have a blue-violet fluorescence.

The resinous product formed in the reduction of benzothiamide contains *stilbene*, which can be isolated by boiling with alcoholic potash and then distilling with steam. F. S. K.

Action of Dichlorether on Naphthol. By J. WISLICENUS and G. ZWANZIGER (*Annalen*, **243**, 165—171).—*Ethenyltri- α -naphthol* is formed by the action of dichlorether on α -naphthol. The crude product is purified by solution in alkalis and reprecipitation by acetic acid. It

is an amorphous, white powder, soluble in acetic acid, alcohol, ether, acetone, and in dilute alkalis. It forms a crystalline triacetyl-derivative, $C_{32}H_{21}Ac_3O_3$. When ethenyltri- α -naphthol is oxidised by ferric chloride, it is converted into a brownish-red colouring matter of the composition $C_{32}H_{22}O_3$. The action of dichlorether on β -naphthol is not analogous to its action on α -naphthol. The product, $C_{22}H_{16}ClO$, crystallises in plates melting at 174° . It resists the action of boiling potash and is not attacked by acetic anhydride. W. C. W.

Terpenes and their Derivatives. By J. W. BRÜHL (*Ber.*, **21**, 145—179).—A comparative study of the chemical and physical properties of the terpenes. A table containing the boiling point, rotation, density d , refractive index for the C line n , specific refraction $\frac{n^2 - 1}{(n^2 + 2)d}$, and molecular refraction $\frac{n^2 - 1}{n^2 - 2} \frac{P}{d}$ (P being the molecular weight), of a number of the best known terpenes, has been compiled from the data of different observers. The terpenes are thus divided into eight groups, similar to those given by Wallach (*Abstr.*, 1887, 965), phellandrene and terpinene coming under the heading laurene, and menthene and sesquiterpene forming an extra group. These groups are:—

1. *Citrene* (limonene), boiling point 172 — 179° , the differences probably due to impurities in the specimens examined. Dextrorotatory. Sp. gr. 0.846. Refractive index 1.47. Specific refraction 0.328. Absorbs 2 mols. HCl, the resulting product being identical with the similar product from dipentene, and giving the latter and not citrene when the hydrogen chloride is removed by means of aniline. From this, and the formation of a tetrabromide melting at 104° , the presence of two unsaturated or double bonds is probable, as also from the molecular refraction which agrees closely with that calculated for such an unsaturated compound.

2. *Dipentene*.—Differs from the above only in being optically inactive and yielding a tetrabromide melting at 124° .

3. *Isopentene*.—Dextrorotatory, differs only slightly from the two former in physical properties.

4. *Sylvestrene*.—Has probably never been prepared in a state of purity, and does not appear to differ in any marked degree from the foregoing.

5. *Pinene*.—Boiling point 155 — 160° . Sp. gr. 0.859. Refractive index 1.463. Specific refraction 0.320. The molecular refraction is that of a compound containing one double bond. This agrees with the chemical evidence, as pinene combines with 2 mols. of bromine and 1 mol. HCl.

6. *Laurene and Menthene*.—Boiling point 173 — 175° . Lævorotatory. Resembles pinene in other respects.

7. *Camphene*.—Solid, melting at 47° ; boils at 156 — 157° . The hydrogen chloride derivative is very unstable and is decomposed by water at ordinary temperatures; it is therefore probable that this is only a molecular compound, camphene containing no double bond, a view supported by its optical properties.

8. *Sesquiterpene*, $C_{15}H_{24}$.—Found in volatile oils associated with the

terpenes. Boiling point 250—260°. Rotation differs for different varieties. From its optical and chemical properties appears to contain two double bonds.

The author regards the terpenes as derivatives of paracymene. Formulæ similar to those of Wallach (*loc. cit.*) are proposed for citrene, dipentene, pinene, and phellandrene, and a discussion of the various possible formulæ for the other terpenes is entered into.

H. C.

Specific Rotation of Dextrocamphoric Acid and its Salts.

By W. HARTMANN (*Ber.*, **21**, 221—230).—The specific rotation of dextrocamphoric acid and its salts in solution is represented generally by $[\alpha] = a + bp$ or $A + Bq$, p being the percentage of active substance, q that of the solvent, a the specific rotation for greatest dilution, A that for greatest concentration. The rotation of the free acid in acetic acid, acetone and alcohol varies with the nature of the solvent. The anhydride is optically inactive. The constants in the above equations were determined for solutions of the lithium, magnesium, ammonium, calcium, sodium, potassium and barium salts. By the aid of these constants, the specific rotation of the acid in the salts was calculated, which is more than double that of the free acid, and is nearly equal for all salts for the same dilution. The molecular rotation $M = [\alpha]P/100$, where P is the molecular weight, was also calculated for solutions of the above salts for $p = 0, 5, 10, 15$, and 20. It is found that the molecular rotation is very nearly the same for all salts at the same concentration. Hence also the specific rotation increases with the molecular weight.

H. C.

Alantic Acid and Alantole. By MARPMANN (*Arch. Pharm.* [3], **25**, 826—827; from *Bresl. ärztl. Zeit.*, **5**, 1887).—On distilling the root of *Inula helenium* with water, a distillate is obtained containing helenin, $C_{12}H_{16}O_2$, alantic anhydride, $C_{16}H_{20}O_2$, and alantole, $C_{20}H_{32}O$.

Alantic acid crystallised from alcohol, melts at 91°, and sublimes with loss of the elements of water, becoming alantic anhydride; both compounds are insoluble in water, soluble in alcohol, and with alkalis form salts soluble in water. *Alantole* is an aromatic liquid which boils at 200°, is laevorotatory, and has ozonising properties somewhat similar to those of the turpentine oils. Helenin, alantic acid, and alantole are antiseptics.

J. T.

Oxidation of 1-Quinolinesulphonic Acid. By H. ZÜRCHER (*Ber.*, **21**, 180—182).—Amidosulphobenzoic acid, $[COOH : NH_2 : SO_3H = 1 : 2 : 3]$, is formed in small quantity when 1-quinolinesulphonic acid is oxidised to quinolinic acid by Fischer and Renouf's method (*Abstr.*, 1884, 1049). The yield amounts to about 5 grams from 90 grams of quinoline.

W. P. W.

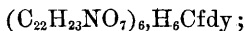
Reactions of the Opium Alkaloids. By P. C. PLUGGE (*Arch. Pharm.* [3], **25**, 793—811).—With potassium chromate, solutions of narcotine salts, both cold and warm, give a precipitate of free narcotine. Papaverine in the cold gives a mixture of chromate and free alkaloid; but with heat free papaverine only. Narceine in cold saturated

solution gives no precipitate, but if hot narceïne chromate and free narceïne come down. Thebaine gives thebaine chromate. Codeïne also gives the corresponding chromate, whilst morphine gives chromate and free morphine.

With potassium dichromate, narcotine, papaverine and thebaine give the corresponding dichromates, narceïne gives the dichromate and free alkaloid. Codeïne in very dilute solution gives the dichromate; stronger solutions afford precipitates which have not yet been examined. Morphine gives a dirty brown precipitate of variable composition.

With potassium ferrocyanide, narcotine hydrochloride gives free alkaloid or a mixture of variable composition; the papaverine salt gives $(C_{20}H_{21}NO_4)_4 \cdot H_4Cfy$; the narceïne salt gives free alkaloid, the hydroferrocyanic acid becomes free; the thebaine salt gives the compound $(C_{19}H_{21}NO_3)_4 \cdot H_4Cfy$; the codeïne salt solution (1 : 70) is not precipitated; the morphine salt solution (1 : 60) is not precipitated.

With potassium ferricyanide narceïne gives the salt



papaverine and thebaine give similar precipitates, narceïne gives free alkaloid, hydrogen ferricyanide also becomes free; codeïne in solution (1 : 70) gives no precipitate; morphine solution (1 : 60) becomes dark coloured and a brown deposit forms after long standing.

J. T.

Quinine Alkaloids. By O. HESSE (*Annalen*, **243**, 131—150).—Quinine tartrate crystallises with 2 mols. H_2O ; it parts with one mol. H_2O at 120° , and the second at 140° . A mixture of quinine and cinchonidine tartrates loses water more easily than quinine tartrate, but if the mixture contains more than 33 per cent. of quinine tartrate, it cannot be thoroughly dried by exposure to a temperature of 120 — 130° . If ammonia is added to a solution of quinine disulphate containing not more than 10 per cent. of cinchonidine disulphate, ether extracts from the mixture the compound $C_{20}H_{24}N_2O_2 + 2C_{19}H_{22}N_2O$. This substance crystallises in rhombohedra, and is decomposed by boiling ether. On recrystallisation from hot dilute alcohol, crystals of the composition $C_{20}H_{24}N_2O_2 + 7C_{19}H_{22}N_2O$ are obtained. The compound $C_{20}H_{24}N_2O_2 + 2C_{19}H_{22}N_2O$ forms a normal sulphate crystallising with 18 mols. H_2O , a normal tartrate containing 6 mols. H_2O , and a normal chromate with 18 mols. H_2O .

The estimation of quinine as chromate as proposed by de Vrij (*Abstr.*, 1887, 404) is open to several objections (*loc. cit.*).

The author confirms the existence of the compound of quinine and conchinine described by Wood and Barret (*Chem. News*, **45**, 6) and he succeeded in preparing a similar compound of quinine and hydroconchinine, $C_{20}H_{24}N_2O_2 \cdot C_{20}H_{26}N_2O_2 + 2\frac{1}{2}H_2O$.

With cinchonidine and homocinchonidine, piperonylic acid forms salts crystallising in needle-shaped crystals soluble in chloroform. The hydrocinchonidine salt is soluble in water and in chloroform. Quinine sulphate is converted into *isoquinine* by solution in strong sulphuric acid. The new base forms a normal sulphate which crystallises in small needles. It does not yield a precipitate with sodium

tartrate. *Isoconchinine* is deposited from ether in needles. The sulphate, $(C_{20}H_{24}N_2O_2)_2 \cdot H_2SO_4 + 8H_2O$, is crystalline, and the platinum-chloride, $C_{20}H_{24}N_2O_2 \cdot H_2PtCl_6 + 3H_2O$, is amorphous. *Isocinchonidine* crystallises in colourless plates, freely soluble in ether and chloroform. It melts at 235° . *Isocinchonine* is freely soluble in ether. On evaporation, the ethereal solution leaves an amorphous residue which soon becomes crystalline.

Hydroconchinine yields a crystalline sulphonic acid,



W. C. W.

Optical Isomerides of Cinchonine. By E. JUNGFLIEß and E. LÆGER (*Compt. rend.*, **105**, 1255—1258).—Pure cinchonine dissolved in four times its weight of a mixture of equal parts of water and sulphuric acid of sp. gr. 1·84, yields a colourless solution which boils at 120° . After boiling for 48 hours, the liquid is amber-coloured, but does not become turbid on cooling. When diluted and made alkaline with sodium hydroxide, it yields an abundant curdy precipitate which soon changes to a porous mass, and gradually hardens. This product contains neither cinchonine nor cinchonidine, but consists of six bases, four of these are isomerides of cinchonine, which form readily crystallisable salts.

Cinchonibine is insoluble in ether, but crystallises from boiling alcohol in prismatic needles. It yields a succinate which forms bulky crystals slightly soluble in cold water. It is dextrogyrate, $[\alpha]_D = +175\cdot8^\circ$, in an alcoholic solution of 0·75 per cent.

Cinchonifine is insoluble in ether, but crystallises from boiling alcohol in highly refractive needles. It is dextrogyrate, $[\alpha]_D = +195\cdot0^\circ$, in an alcoholic solution of 0·75 per cent. The succinate crystallises in needles, and is very soluble.

Cinchonigine is soluble in ether, from which it crystallises in prisms, and is levogyrate, $[\alpha]_D = -60\cdot1^\circ$, in an alcoholic solution of 1 per cent. It yields a distinctly crystalline hydrochloride slightly soluble in water.

Cinchoniline is soluble in ether, and forms very bulky crystals. It is dextrogyrate, $[\alpha]_D = +53\cdot2^\circ$, in an alcoholic solution of 1 per cent. The hydrochloride forms large crystals which are very soluble; the dihydriodide is insoluble. These four compounds increase the number of isomerides of the composition $C_{19}H_{22}N_2O$ to seven.

The other two bases are isomeric one with another, but belong to another group. They are products of oxidation produced with intermediate formation of a sulphonic derivative which is decomposed by water.

α -*Oxycinchonine*, $C_{19}H_{22}N_2O_2$, forms prismatic needles insoluble in ether but soluble in dilute alcohol. It is dextrogyrate, $[\alpha]_D = +182\cdot56^\circ$, in an alcoholic solution of 1 per cent. Its salts with the hydracids are only slightly soluble.

β -*Oxycinchonine*, $C_{19}H_{22}N_2O_2$, is insoluble in ether, but dissolves in dilute alcohol, and crystallises in needles arranged in spherical groups. It is dextrogyrate, $[\alpha]_D = +187\cdot14^\circ$, in an alcoholic solution of 1 per cent. Its salts with hydracids are very soluble.

C. H. B.

Cocaine. By A. EINHORN (*Ber.*, **21**, 47—51).—The ethereal salts of benzoylecgonine can be obtained by passing hydrogen chloride into its alcoholic solution; the ethyl, propyl, and isobutyl salts were prepared in this way; they have already been described by Merck (*Abstr.*, 1886, 163).

Succinic acid is formed when anhydroecgonine or ecgonine is oxidised with potassium permanganate; 10 grams of ecgonine hydrochloride yield about 2.2 grams of succinic acid. Ecgonine hydrochloride also gives succinic acid when it is boiled for some time with nitric acid; from 2 grams of the salt, about 1 gram of succinic acid is obtained.

The atomic complex, $C \cdot CH_2 \cdot CH_2 \cdot C$, which is contained in succinic acid, must originate from the reduced pyridine-ring of the cocaine-derivative, and the formation of succinic acid shows that the side-chain is either in the α - or β -position.

Nitrogenous compounds are also formed in the oxidation of ecgonine and anhydroecgonine. F. S. K.

Physiological Chemistry.

Behaviour of Congo-red with Human Urine and with Acid Salts. By E. BRÜCKE (*Monatsh. Chem.*, **8**, 632—637, compare *Abstr.*, 1887, 986).—Human urine and a solution of ammonium acetate containing free acetic acid give similar tints with Congo-red. The addition of magnesium sulphate, however, in no way affects the colour of the former, whilst it causes the latter to darken rapidly with the formation of a brownish-black precipitate. The acid tartrates of ammonium and potassium give with Congo-red a beautiful violet colour. The author sees no reason to change the conclusion he draws from previous experiments with Congo-red, that human urine contains no free acid. G. T. M.

Chemistry of Vegetable Physiology and Agriculture.

Colour of Leaves in Relation to the Assimilation of Carbon.

By T. W. ENGELMANN (*Ann. Agronom.*, **13**, 477—480; from *Bot. Zeit.*, 1887, 25—29).—The yellow leaves of an elder bush were studied side by side with the green leaves of the same plant by means of Engelmann's microspectral photometer, and by their behaviour towards aerobic bacteria.

The absorption-spectrum of the living yellow cells shows that the bands II and III in the orange and the yellow-green which belong to the green colouring constituent (cyanophyll or pure chlorophyll), and

which are absent from the spectrum of xanthophyll, are scarcely indicated.

In the spectrum of the green living cells, on the other hand, these bands are easily identified, although Reinke, working with Glan's photometer, did not succeed in finding them. It would thus appear that the yellow cells contain little chlorophyll proper, or chlorophyllane, and it would be expected that they should lack the power of assimilation. By immersing equal areas cut out of the yellow and green leaves in a liquid charged with aërobic bacteria, and exposing the liquid to the light, it is easily seen that the yellow cells disengage far less oxygen in a given time than the green cells, and hence it is probable that if they contained pure xanthophyll only, the assimilating power would be *nil*.

With reference to the plants in which the light reaches the granules of true green chlorophyll through layers of cells coloured red or purple (copper-beech, red cabbage, &c.), the author observes that they do not differ from what is observed in green plants either in the disposition of the chlorophyll granules or in their size, or the nature or intensity of their colour. Moreover, the red varieties of a plant, for example, *Coleus*, are quite as large and vigorous as the green specimens. It follows that the red colouring matter of these plants can only absorb those rays which have little influence on assimilation.

The colouring matter is always a red-purple, which has most effect in absorbing the green rays, whilst red rays pass freely, and blue and violet very well. The curve of absorption rises about the middle of the spectrum, and descends again at the other end. When the solution is very concentrated a large absorption-band is seen between the wave-lengths $\lambda = 0.59\mu$ and $\lambda = 0.50\mu$. Speaking generally, the absorption of light is complementary to that caused by solutions of chlorophyll. If, as was formerly believed, the maximum of assimilation corresponded with the yellow rays, that process would be much impeded in the red plants, for the yellow rays are enfeebled to the extent of one-third in passing through the red solution.

J. M. H. M.

Supply of Food Constituents at Different Periods of Plant Growth. By G. LIEBSCHER (*Bied. Centr.*, 1887, 658—660).—As a basis for the science of manuring, the author advances a new theory. The view sometimes held, that one species of plant has a greater power than another of taking up some particular food constituent cannot be reconciled with the laws of osmosis; but the difficulties met with can be explained in another way. Each day the root should supply a certain amount of food to the plant; this amount varies more or less at different stages of growth, and further, these variations differ in the case of different plants; thus one species requires a fairly uniform daily supply throughout its period of growth, whilst another requires much more at one stage than at another. From the composition of various plants at different stages of growth, the author has constructed a number of curves showing how these supplies vary. Such information affords an important clue to the proper manuring of a particular species; thus for a plant requiring a uniform daily supply, a slowly decomposing and lasting manure is appropriate;

whilst an easily soluble one should be given to a plant whose demand is large during a short period.
H. H. R.

Wheat Experiments in 1887. By A. LADUREAU and MOUSSEAU (*Ann. Agronom.*, 13, 538—551).—The experiments were carried out on the poor lands of the Brie district, and had for their object to demonstrate the utility of artificial manures, and to ascertain the most productive and economical manuring for the district. The soil, limed in 1885, contained only 0·084 per cent. N, 0·085 per cent. P_2O_5 , 0·325 per cent. K_2O , and 0·280 per cent. CaO .

One variety of wheat (Golden Drop) was sown on all the plots, on the same day, October 11th, 1886, at the uniform rate of 2 hectolitres per hectare; each plot measured 3 ares. Both straw and grain were weighed on each plot, the value calculated out at the price actually realised, and compared with the expense of the various manures used. The yield varied from 950 kilos. per hectare of grain, and 1550 kilos. straw on the unmanured plot, to 3200 kilos. grain and 5650 kilos. straw on the best plot, which was manured with 50 cubic metres farmyard manure, and 300 kilos. of 15 per cent. superphosphate per hectare in the autumn, and top dressed with 250 kilos. sodium nitrate in the spring. The increase obtained on this plot over the unmanured plot exceeded the cost of the manures applied by 319·75 francs per hectare. A still more favourable result (although from a smaller crop) was obtained on the plot dressed with 100·5 kilos. P_2O_5 in superphosphate and 48·5 kilos. of ammoniacal nitrogen per hectare in the autumn, 29·75 kilos. nitrogen as sodium nitrate per hectare in the spring; on this plot, the increase obtained by the manure exceeded the cost of the latter by 389·4 francs per hectare. The results obtained on all the plots justify the following conclusions:—

1. Superphosphate applied at the rate of 50 kilos. per hectare produces an increase of crop on these soils.

2. Ammonium sulphate applied in spring gives results greatly superior to those given by the same money value of sodium nitrate.

3. Basic cinder substituted for some of the superphosphate did not give good results. The authors are now trying basic cinder alone, and expect to get better results with it. That employed in the present series of experiments was very coarsely ground.

4. Farmyard manure alone did not even repay its cost, a result probably due to the exceptional drought of the season. The authors recommend the wheat growers of this district to sell their farmyard manure to the vine growers, and with a portion of the proceeds to buy artificial manures.

J. M. H. M.

Experimental Culture of Sugar-beet at Grignon in 1887. By P. P. DEHÉRAIN (*Ann. Agronom.*, 13, 529—535).—The experiments were to decide two points, namely, the quality of the seed obtained at Grignon from previous crops of Vilmorin's sugar-beet, and the effect of farmyard manure as compared with mineral manures on the yield of sugar. The plots sown with the Grignon seed were therefore compared with parallel plots sown with seed obtained direct from Vilmorin; the manures tried were farmyard manure, sodium nitrate, and

ammonium sulphate; and the quality of the roots from the various plots was ascertained by selecting proportionate numbers of large, medium, and small roots from each plot, and testing the juice by the hydrometer and in the saccharimeter. The chief results of the experiments are that the continuously unmanured plots of both series yielded very small crops of small roots poor in sugar, namely, 13900 and 10100 kilos. of roots per hectare, density of juice 6·9 and 7·2, percentage of sugar in juice 15·8 and 14·6. The mean percentage of sugar in the juice of the roots from the Grignon seeds was 17·7, and in the juice of the roots from the Vilmorin seeds 17·1, so that it is evident a good sample of seed may be relied on by the farmer for at any rate a second harvest. Both series of plots proved that on the light soil of Grignon, moderate dressings of farmyard manure, with or without the addition of sodium nitrate or ammonium sulphate, produced considerably larger crops than the sodium nitrate or ammonium sulphate alone, and that the roots grown with the farmyard manure were by no means poor in sugar, the juice containing 18 to 19·5 per cent.; 30000 kilos. farmyard manure per hectare, or 20000 kilos. with 200 kilos. sodium nitrate, were found to be the best dressings; a larger quantity of farmyard manure diminished the crop, and ammonium sulphate proved, as it generally has done at Grignon, decidedly inferior to sodium nitrate.

J. M. H. M.

Iron in Wine. By SAMBUC (*J. Pharm.* [5], 16, 344—345).—A wine from Seyne (Var.) from an American vine, the Jacquez, was found to contain, per litre :—Alcohol, 67·54 grams; dry extract at 100°, 20·50; acidity in terms of sulphuric acid, 6·20; total ash, carbonated, 2·60; anhydrous ferric oxide, 0·11. The iron was determined both gravimetrically and volumetrically. The usual amount of iron in wines is equivalent to 0·01—0·02 gram of ferric oxide.

J. T.

Nitrates in Soils and Water. By E. BRÉAL (*Ann. Agronom.*, 13, 561—568).—The author has applied the mode of detecting nitrates described in a previous memoir (*Abstr.*, 1887, 1138) to the study of the arable, pasture, and forest soils, and the waters in the neighbourhood of Baden, Switzerland. A few cubic centimetres of the sulphophenol reagent in a stoppered bottle, and some strips of prepared filter-paper, are sufficient to show that nitrates are abundant in the arable soils, deficient in the meadow soils, and almost absent from the forest soils. He attributes the deficiency in the last two descriptions of soil to the excess of organic matter hindering nitrification, and to the rapid consumption of what nitrates are formed by the perennial crops. The mountain streams are free from nitrates, and so is the water of a hot mineral spring highly charged with sulphate of lime.

J. M. H. M.

Sulphur and Phosphorus in Plants, Soils, and Moulds. By BERTHELOT and ANDRÉ (*Compt. rend.*, 105, 1217—1222).—Sulphur may exist in plants, soils, and moulds, in the form of sulphates directly precipitable as barium sulphate; in the form of compounds analogous to the ethyl sulphates from which the sulphur is obtained

as sulphate by hydrolysis or oxidation; in the form of salts such as sulphides, sulphites, and thiosulphates, which can be converted into sulphates by oxidation in solution; and in the form of carbon-compounds such as taurine, cystin, albumin, &c., the sulphur in which is not converted into sulphate by oxidation in solution.

In order to estimate the total sulphur or phosphorus, the substance previously dried at 100° is burnt in a current of oxygen in a glass tube, the products of combustion being conducted through a column of pure anhydrous sodium or potassium carbonate. Care must be taken that the temperature does not rise sufficiently high to fuse the alkaline carbonates in the ash. When combustion has ceased, the current of oxygen is continued for some time in order to convert any alkaline sulphides into sulphates. The contents of the tube are dissolved in water, acidified with hydrochloric acid, and precipitated with barium chloride. In the filtrate from the barium sulphate, the phosphorus is precipitated by means of ammonium molybdate, and is afterwards converted into magnesium pyrophosphate.

The soil examined contained 1.418 gram of sulphur per kilo., but 1 per cent. hydrochloric acid only extracted one-seventh of this, and concentrated nitric acid dissolved very little more.

The mould contained 6.156 grams of sulphur per kilo., of which 0.947 gram was soluble in cold dilute hydrochloric acid, and 2.0213 in concentrated boiling nitric acid.

One of the specimens of the plant, *Mercurialis annua*, contained 10.768 grams of sulphur per kilo., 3.040 being soluble in cold dilute hydrochloric acid. Another specimen contained 6.584 grams per kilo., 2.834 grams being soluble in cold 1 per cent. hydrochloric acid and 4.554 in boiling concentrated nitric acid.

The sulphur existing as sulphate is in all three cases only a small proportion of the total quantity, and the sulphur convertible into sulphate by oxidation in solution, although greater, is still only a fraction of the total amount.

Phosphorus may exist in plants, moulds, and soils, as phosphates soluble in water or acids; as ethereal compounds yielding phosphates on hydrolysis or oxidation; as phosphides or phosphites, &c., which can be oxidised to phosphates in solution; and as organic compounds which cannot be converted into phosphates in the wet way.

The soil examined contained 0.641 gram of phosphorus per kilo., 0.134 gram of which was soluble in hydrochloric acid of 1 per cent., 0.420 in hydrochloric acid of 10 per cent., 0.603 in boiling concentrated nitric acid. The total phosphorus is much greater than that existing as phosphate, and it is not completely oxidised by nitric acid.

The mould contained 3.091 gram per kilo., 2.328 being soluble in cold dilute hydrochloric acid, and 3.085 in hot concentrated nitric acid. In this case, the proportion of phosphate is very large, and it is noteworthy that concentrated nitric acid removes the whole of the phosphorus. This last result is, however, probably abnormal.

The first specimen of the plant contained 2.812 grams of phosphorus per kilo., 1.668 gram being soluble in cold dilute hydrochloric acid. The second specimen contained 5.440 gram per kilo., 2.963 being soluble in cold dilute hydrochloric acid, and 4.154 in hot con-

centrated nitric acid. The proportion of phosphorus depends largely on the age of the plant. The last specimen contains twice as much as the mould, and nine times as much as the soil. The proportion of soluble phosphates is greater than in the soil, and is comparable with that in the mould.

From these results, it is evident that sulphur and phosphorus, like nitrogen, exist in plants, moulds, and soils, in several different forms.

C. H. B.

Analytical Chemistry.

Polaristrobometric Analysis. By H. LANDOLT (*Ber.*, **21**, 191—220).—The specific rotation of nearly all circularly polarising solutions may be expressed in terms of—(1.) The percentage q of the inactive solvent, $[\alpha] = A + Bq + Cq^2$. (2.) The percentage p of the active substance, $[\alpha] = a + bp + cp^2$. (3.) The concentration c , $[\alpha] = A_1 + B_1c + C_1c$. In many cases, the third term may be neglected. The two last equations may be used for either concentration or percentage composition, since $c = pd$, where d is the specific gravity of the solution.

In determining from the rotation the amount of substance in solution, the following cases have to be distinguished:—

I. A solution may contain a single active substance in an inactive solvent. This is the most general case, and the specific rotation is as a rule constant, that is, the angle of rotation is proportional to the concentration, as is the case for aqueous solutions of cane-sugar, milk-sugar, maltose, raffinose, dextrose, lævulose, invert sugar, and galactose. The specific rotation is, however, not always constant, but sometimes a linear function of the concentration, as, for instance, for solutions of nicotine and camphor in alcohol.

II. Solution of an active substance in two inactive solvents. The specific rotation of nearly all active substances being unequally influenced by different solvents, the action of each solvent alone on the rotation has to be separately considered. These will be $[\alpha] = A + Bq$ and $[\alpha]_1 = A + B_1q$, the constant A being the rotation of the pure active substance and the same in each case. Hence if q and q_1 are the weights of two solvents contained in 100 parts of the mixture, the specific rotation will be $[\alpha]_m = A + Bq + B_1q_1$. This presupposes each solvent to act perfectly independently of the other, which, however, only happens in the case of cane-sugar, the rotation of which is the same for all solvents. In other cases, the value of $[\alpha]_m$ lies irregularly between $[\alpha]$ and $[\alpha]_1$, as, for instance, for narcotine in 1 vol. alcohol to 2 vols. chloroform, or it attains a maximum higher than either $[\alpha]$ or $[\alpha]_1$, as for cinchonidine in the above solvents or cinchonidine nitrate and hydrochloride in mixtures of alcohol and water.

III. Solution of two active substances in an inactive solvent.

Firstly, the combined weight of the two substances in 100 c.c. solution may be known. Let the specific rotation of the solution be $[\alpha]$, and the mixture contain x per cent. of one constituent of the specific rotation $[\alpha]_x$, and $y = 100 - x$ of the other constituent of the specific rotation $[\alpha]_y$. Then $[\alpha]_x x + [\alpha]_y (100 - x) = 100 [\alpha]$, from which x and y are obtained in terms of $[\alpha]$, $[\alpha]_x$, and $[\alpha]_y$. Instances of this are solutions of cane-sugar and raffinose and quinine and cinchonine sulphates. Secondly, the combined weight of the two active substances may be unknown, and the analysis is then effected by measuring the rotation of the solution, and converting one or both of the constituents into another optically active substance by inversion, and again measuring the rotation. If only one constituent undergoes inversion, if ϕ_1 and ϕ_{11} the angles of rotation for unit concentration of each constituent be known, ρ the rotation of the inverted substance, and c_1 and c_{11} the concentrations required, we have—

$$\text{Before inversion, } \phi_1 c_1 + \phi_{11} c_{11} = \alpha$$

$$\text{After inversion, } \rho k c_1 + \phi_{11} c_{11} = \alpha$$

from which c_1 and c_{11} may be calculated. This is true for solutions of cane-sugar and invert sugar and cane-sugar and dextrin, the cane-sugar being the substance inverted. If both constituents undergo inversion, then if ρ_{11} is the rotation of the second inverted substance—

$$c_1 = \frac{\rho_{11}\alpha - \phi_{11}\alpha_1}{\rho_{11}\phi_1 - \rho_1\phi_{11}} \text{ and } c_{11} = \frac{\rho_1\alpha - \phi_1\alpha_1}{\rho_{11}\phi_{11} - \rho_1\phi_1}.$$

This is true for a solution of raffinose and cane-sugar.

IV. Analysis of inactive substances in solution. This would be effected by measuring the influence of certain inactive substances on substances of known rotation, such, for instance, as the action of boric acid on tartaric acid solutions. Little has been done in this direction, and no attempt at formulating the above influence can at present be made.

H. C.

Correct Analysis of Superphosphates. By J. RUFFLE (*J. Soc. Chem. Ind.*, 6, 491—494 and 704—705).—In furtherance of his investigations on moisture and free acid in superphosphates (this vol., p. 87), the author suggests the following method of analysing superphosphates:—(1.) Moisture: estimated by calcium chloride in a vacuum. (2.) Soluble phosphoric acid: estimated by direct determination. (3.) Insoluble phosphate: estimated by direct calculation from the amount of insoluble phosphoric acid after evaporation to dryness with hydrochloric acid and re-solution with hydrochloric acid. (4.) Calcium sulphate: estimated by determining the whole sulphuric acid present and calculating this into anhydrous calcium sulphate. (5.) Sand: estimated by evaporating to dryness with hydrochloric acid and re-solution in hydrochloric acid. (6.) Combined water and organic matters, including the uncombined calcium oxide: estimated by difference. (7.) Alkalis, magnesia: amounts as determined.

By this plan no more work is introduced than is practised at

the present time, whilst the statements 1, 2, 3, 4, 5, and 7 will be true from direct determination, and the commercially unimportant "combined water and organic matter" will not be attempted; hence false statements will be avoided.

The author is of opinion that the calcium oxide existing as mono-calcium phosphate in ammoniated phosphates may be wholly passed over, and the total calcium oxide, less the amount of the insoluble phosphate, be calculated out to calcium sulphate. D. B.

Separation of Zinc from Nickel and Manganese and Estimation of Nickel. By T. BAYLEY (*J. Soc. Chem. Ind.*, 6, 499).—A good separation of zinc from nickel and from manganese may be made in a hot solution containing free phosphoric acid by precipitation with hydrogen sulphide. Cobalt has a tendency to go down in small quantity with the zinc. In order to precipitate nickel from solutions, the author recommends the addition of ammonium sulphide until the last drop renders the liquid alkaline; this is followed by ammonium benzoate, and afterwards by a few drops of hydrochloric acid. In this solution, the nickel is completely precipitated as sulphide. The latter is heated in a porcelain dish, dissolved in nitric acid, evaporated, ignited, and weighed as sulphate. The ignition should be effected at a low red heat, and the dish allowed to cool. The sulphate is then treated with sulphuric acid and submitted to a further short ignition. Success would appear to depend on the shortness of the second ignition.

D. B.

Reaction of Iron with Nitric Acid. By T. BAYLEY (*J. Soc. Chem. Ind.*, 6, 499–500).—When an assay of "nitre" in sulphuric acid is made in the nitrometer, an error is caused by absorption of nitric oxide when the acid contains iron. Nitric oxide, shaken with mercury and pure sulphuric acid, suffers no absorption, nor does mercury pass into solution in the acid unless the acid contains a small quantity of iron. On copiously diluting the acid by the addition of air-free water, and subsequently adding a solution of a ferricyanide to the cooled acid liquid, the blue reaction is readily obtained. The mercury seems to take no part in the reduction of the ferric salt, since the results can be equally well obtained if pure nitric oxide is passed through a set of Geissler bulbs charged with sulphuric acid containing ferric sulphate. The sulphuric acid in this case, as in the nitrometer, assumes a purple tint, which is characteristic of the reaction when it takes place in the acid, but not in the aqueous solution.

D. B.

Action of Oils on Polarised Light. By W. BISHOP (*J. Pharm.* [5], 16, 300–301).—Besides resin and castor oils, there are two others which very perceptibly affect polarised light. Thus in a tube of 20 cm. long colza oil gave a rotation of -1.6° to -2.1° , and sesame oil gave from $+3.1^\circ$ to 9.0° . Of several other vegetable oils examined none gave as much as 1.0° . In the case of certain linseed oils, when found to have dextrorotative power, they should be examined for sesame oil before concluding that resin oil has been added.

J. T.

General and Physical Chemistry.

Dispersion Equivalents. By J. H. GLADSTONE (*Proc. Roy. Soc.*, **42**, 401—410).—This paper is a continuation of the author's researches on dispersion equivalents. Notwithstanding the difficulties of the investigation, the following conclusions have been arrived at:—

1. That dispersion, like refraction, is primarily a question of atomic constitution.
2. That dispersion, like refraction, is modified by profound differences of constitution, such as change of atomicity.
3. That dispersion frequently reveals differences of constitution, at present unrecognised.

The following dispersion equivalents ($H-A$) have been determined:—Phosphorus (liquid), 3·0; sulphur (double bond), 2·6; sulphur (single bonds), 1·2; hydrogen, 0·04; carbon, 0·26, 0·51, and 0·66; oxygen (double bond), 0·18; oxygen (single bonds), 0·10; chlorine, 0·50; bromine, 1·22; iodine, 3·65; nitrogen, 0·10; CH_2 , 0·34; NO_2 , 0·82. The values for CH_2 , H , and C are worked out in the same way as the refraction equivalents. In unsaturated compounds, the dispersion equivalent is much greater, (0·5) in allyl compounds and olefines, and at least 0·8 in the aromatic series. Where the carbon has all four bonds satisfied with carbon-atoms (with refraction value 6·0), the dispersion equivalent is enormously increased. In considering the dispersion equivalents of solutions of metallic salts, it is pointed out that where the solution is dilute the values are untrustworthy, owing to the smallness of the specific dispersion, the values for potassium and sodium alone are therefore considered. The difference between the dispersion equivalents of their salts is 0·09. In determining the value for potassium itself, the haloïd salt was rejected, as it was anticipated that the chlorine value might be higher than it is in organic compounds, as is the case with the refraction equivalents. Determined from the formate and acetate, with the values given above for carbon, hydrogen, and oxygen, the dispersion equivalent for potassium is 0·53 and 0·44 for the salts respectively. From potassium hydroxide viewed as water, with a hydrogen-atom replaced, the value 0·565 is obtained. From the nitrite, by subtracting the value for NO_2 , 0·48 is obtained. From the cyanide, 0·58; from the carbonate, 0·40; from the oxalate, 0·59. These variations cannot be due to experimental error, nor is it probable that potassium has more than one dispersion equivalent, as it has only one refraction equivalent. The uncertainty probably lies in the value of the radicles to which the metal is joined.

H. K. T.

Mathematical Analysis of the Spectra of Magnesium and Carbon. By A. GRÜNWALD (*Monatsh.*, **8**, 650—712).—In accordance with the principle laid down by the author (*Abstr.*, 1887, 1070), an analysis of the spectra of magnesium and carbon has been effected, the data of different observers, chiefly those of Liveing and Dewar, being used for this purpose.

The magnesium spectrum is found to show the presence of the primary substance *c* in the same condition in which it is found in oxygen and carbon, of the primary substance *b* in the state in which it exists in free hydrogen, and in the more condensed state in which it is found in the water-vapour spectrum, and also of *b* (helium) in an uncondensed state. Besides these, a number of very weak, and at present unknown hydrogen and oxygen lines are present.

The spectrum of carbon contains the primary substance *c* in the state in which it is found in oxygen and magnesium, and also the substance *b*. This latter exists in four different conditions: in the state in which it is observed in free hydrogen; in the state in which it exists in the hydrogen of water-vapour; and in a more dilated chemical condition, and a more condensed condition than that in which it occurs in free hydrogen. A number of hydrogen and oxygen lines are also present, most of them very weak, but which, on multiplying their wave-lengths by the factor $\frac{2}{3}$, as in the case of those in the magnesium spectrum also, are converted into lines in the water spectrum.

H. C.

Compounds of the Rare Earths yielding Absorption-spectra. By G. KRÜSS and L. NILSON (*Ber.*, **21**, 585—588).—A rejoinder to Bailey (this vol., p. 208).

Contact Electricity. By W. v. ULJANIN (*Ann. Phys. Chem.* [2], **33**, 238).—The author points out that Exner (this vol., p. 208) has misunderstood his method (*Ann. Phys. Chem.* [2], **30**, 699) of determining the potential difference between zinc and copper, as he appears to have assumed that the author covered a copper cylinder with a zinc one, and inserted such a fraction of a Daniell, that when the latter cylinder was removed there was no deflection of the electrometer. This arrangement would clearly not enable the potential difference to be measured, as it would require that the envelope also should be at the same potential, and the latter is determined by that of the walls of the room.

In the arrangement used, the two cylinders were of zinc, and were surrounded by a copper envelope, and before removing the outer cylinder it was separated from the inner one. Then assuming the two zinc cylinders to be at the same potential, there would be no deflection if the copper envelope was at the same potential. This condition was satisfied by the introduction of a certain fraction of a Daniell in the earth connection of the envelope.

It is clear that the method would not serve to determine any potential difference between the zinc cylinders, as it depends on the assumption that they are at the same potential, being of the same metal, and in contact.

G. W. T.

Maximum Galvanic Polarisation of Platinum Electrodes in Sulphuric Acid. By C. FROMME (*Ann. Phys. Chem.* [2], **33**, 80—128).—The great discrepancies between the different determinations of the maximum polarisation in a voltmeter containing dilute sulphuric acid with platinum electrodes, induced the author to investigate

the circumstances on which the amount of polarisation depends. *A priori*, the polarisation might be expected to depend on the nature of the surface of the electrodes, on their dimensions, on the concentration of the acid, and on the pressure at which the gases are liberated.

The concentration of the acid in the different experiments varied from 0.18 to 65 per cent.

The author finds that the manner in which the amount of polarisation varies with the concentration is most complicated in the case of very dilute solutions, for, as the concentration is gradually increased, the polarisation at first increases and reaches a maximum, and afterwards falls to a minimum; when the anode is small, it passes through a second maximum and minimum, until it finally increases steadily with the concentration; with a larger anode, only a single maximum and minimum are observed.

In very dilute solutions, the amount of polarisation is found to depend on whether the water used is distilled in glass or in metallic vessels, this being doubtless due to the presence of small particles of glass or of metal in the distilled water.

When the cathode is small, its surface becomes blackened by the passage of the current, whilst a larger cathode is not sensibly altered.

With the more dilute solutions, and when both the electrodes were small, a yellow deposit was observed on the anode. The black deposit remains unaltered after treatment with concentrated sulphuric acid, but it is slowly dissolved by aqua regia. It can also be removed by reversing the current for some time, or it can be scraped off. This deposit had already been observed by de la Rive (*Ann. Phys. Chem.*, **41**, 156; **45**, 421) and by Poggendorff (*ibid.*, **61**, 605), and their experiments showed that it consisted of platinum in a state of powder, mechanically detached from the cathode. In some of the experiments, even when the cathode is larger, a greyish-brown deposit was observed on the latter, but only when the water had been distilled in glass vessels, from which the author concludes that it was due to particles of glass. It was easily dissolved by concentrated sulphuric acid.

In the case of the larger anodes, a dark yellow coloration was observed after some time. This yellow deposit on the anodes was unaffected by treatment with hot concentrated sulphuric acid or aqua regia, and it occurred whether the water had been distilled in glass or in metallic vessels. The author was unable to determine its cause, but concluded that it was not due to the presence of any impurity in the solution. The amount of polarisation is found to depend on the size of the electrodes; with dilute solutions, the size of the anode is the more important, with stronger ones that of the cathode.

With the solutions used containing, as previously stated, from 0.18 to 65 per cent. of acid, the E.M.F. of polarisation varied from 1.94 to 2.43 of a Daniell when the cathode and anode were both large; from 1.45 to 2.98 when the cathode was small and the anode large; from 1.90 to 4.18 when both cathode and anode were small; and from 1.89 to 4.31 when the cathode was large and the anode small. The least variation, therefore, occurs when both the electrodes are large, and the greatest when the cathode is large and the anode small.

The resistance of the voltmeter when traversed by a strong steady

current diminishes as the concentration of the acid increases, and ultimately reaches a minimum value when the concentration is about the same as that for which the conductivity is found to be a maximum by observations with alternate currents; after this, it increases with further increase in the concentration. When, however, the anode is small, the resistance continues to diminish up to the highest limits of concentration used in the experiments.

G. W. T.

Electromotive Forces of Metals in Cyanide Solutions. By S. P. THOMPSON (*Proc. Roy. Soc.*, **42**, 387—389).—The electromotive forces of copper and zinc in cyanide solutions are examined in order to ascertain the cause of the possibility of depositing these two metals simultaneously. It is found that with higher concentration, the E.M.F. of copper increases more than that of zinc; moreover, in a cold dilute solution of potassic cyanide the E.M.F. of zinc is higher than that of copper, whilst in a boiling saturated solution the E.M.F. of copper is greater than that of zinc: hence it is possible to construct a battery consisting of one metal, copper, and one electrolyte, a solution of potassic cyanide, the anode being kept hot and the cathode cold. Tables are given showing the E.M.F.'s of various metals compared with carbon in cyanide solutions of various strengths. Maxima are frequently found at intermediate stages of concentration. In a mixed solution of copper and zinc cyanides, there is a neutral condition, in which the E.M.F.'s of zinc and copper are equal, depending on the relative amounts of metal, the concentration of the solution, and the temperature. The E.M.F. of the copper is the most sensitive, especially to variations in the concentration of the solution. At the cathode, the concentration is determined, on the one hand, by the rapidity with which the metal is deposited, that is, by the current-density; on the other, by the rapidity of diffusion; hence there will be a certain current-density at which the solution will be maintained in the neutral condition and the metals be deposited equally.

H. K. T.

Resolution of the Electromotive Forces of Galvanic Elements. By J. MIESLER (*Monatsh.*, **8**, 713—720).—In continuation of his work on this subject (this vol., p. 330), the author has examined Marié-Davy, de la Rue, and Niaudet cells, and in each the sum of the potential differences in the various parts of the cell is found to be equal to the total E.M.F. Accumulators were examined, and for these the above was also found to be true. On discharging an accumulator and measuring the potential differences at different intervals, as the total E.M.F. decreased to about one-half of its original value, the potential difference between the negative plate and acid also diminished, but that between the positive plate and acid remained the same. After the cell had been short circuited for some time, the exact opposite had, however, taken place, for the potential difference between the negative plate and acid was still the same, whilst that between the positive plate and acid had decreased. An attempt mechanically to construct an accumulator that should give the same potential differences as a charged accumulator failed.

H. C.

Thermal Alteration in a Daniell Cell and in an Accumulator. By G. MEYER (*Ann. Phys. Chem.* [2], **33**, 265—289).—Investigations have been made on the thermal changes in a Daniell cell by Lindig (*Ann. Phys. Chem.*, **123**, 1), Voller (*ibid.*, **149**, 394), and v. Helmholtz (*Ber.*, **18**, 22), and the latter has shown that in a zinc sulphate cell the temperature-coefficient depends on the degree of concentration of the solution. The object of this paper is to determine more fully on what circumstances the temperature-coefficient depends, in the case both of sulphuric and zinc sulphate cells, and to determine whether the temperature-coefficient of the cell is equal to the sum of the temperature-coefficients at each contact of unlike substances.

In order to ensure their purity, the metals used were obtained by electrolytic deposition from copper sulphate and zinc sulphate, and the copper sulphate, zinc sulphate, and sulphuric acid were chemically pure. The metals and liquids composing the cell were contained in a glass tube of special construction, and the liquids were separated by parchment-paper; the dissolved air being got rid of by use of an air-pump. The measurements of the E.M.F. were always made with a quadrant electrometer, so that there was no polarisation, and the electrometer reading was taken directly after the zinc was introduced into the liquid, to prevent a coating of hydrogen being formed, at the higher temperatures, by the action of the sulphuric acid on the amalgamated zinc. The results obtained with the cells were as follows:—The E.M.F. of a Daniell cell with sulphuric acid increases with the temperature, and the value of the temperature-coefficient depends on the degree of concentration of the liquids in the cell, increasing with an increase in the concentration of the sulphuric acid, until the solution contains about 30 per cent. of the acid, when it attains a maximum value, and diminishes when the concentration is increased beyond this point. The temperature-coefficient increases continuously without attaining a maximum as the concentration of the copper sulphate is increased.

In the case of a zinc sulphate cell, the E.M.F. diminishes as the temperature rises, and when the concentration of the zinc sulphate is increased from a low degree the temperature-coefficient falls to zero, and as the concentration is further increased this has a continually increasing negative value. The effect on the temperature-coefficient of varying the concentration of the copper sulphate solution is the same as in the case of the sulphuric acid cell.

In the accumulator, the temperature-coefficient was found to increase with increased concentration of the sulphuric acid, but the author has not yet been able to determine whether the degree of concentration has any effect on the E.M.F., as the latter begins to diminish as soon as the charging current is discontinued, at first rapidly, and then slowly, but not slowly enough to enable any conclusions to be drawn from the measurements of E.M.F., each of which occupied about six minutes.

During the experiments on the accumulator, whilst evolution of gas was observed from the lead plates when it was placed under the air-pump to free the sulphuric acid from dissolved air, it was found

by depositing lead by means of zinc from a solution of lead acetate, and heating it in a vacuum, that finely divided lead absorbs about 0.206 of its volume of hydrogen. The absorption of air by the accumulator plates would be too small to have an appreciable effect on the E.M.F.

The author, however, found it impossible to obtain any trustworthy results from a cell containing platinum instead of copper, owing to the dependence of the E.M.F. on the amount of air absorbed by the platinum.

G. W. T.

Determination of the Specific Inductive Capacities of Conducting Liquids. By E. COHN and L. ARONS (*Ann. Phys. Chem.* [2], **33**, 13—31).—In a previous memoir (*ibid.* [2], **28**, 454), the authors gave a means of determining the specific inductive capacity of a conducting liquid founded on the result obtained by them that the dielectric polarisation and conduction are mutually independent. In the former experiments, the highest conductivity did not exceed 4.5×10^{-13} in terms of mercury, and the values of the sp. ind. cap. were found to be of much the same magnitude as for good insulators, being in every case less than 5. In the present paper, liquids of higher conductivity are considered, and this made it necessary to devise a new method, as the former one, depending on observations of the rate of leakage of an electrostatic charge, would have required the observations of intervals of time considerably less than the millionth of a second.

The method used for the present inquiry is a modification of Silow's (this Journal, 1876, ii, 267), founded on the principle that when a system of conductors immersed in a homogeneous medium is maintained at a constant potential, the work done against electrical forces, in effecting a given change of configuration, is proportional to the sp. ind. cap. of the medium. The needle and one pair of quadrants of an electrometer were joined to one extremity of the secondary of an induction coil, and the remaining pair to the other extremity. Readings were then taken alternately with the liquid and with air only in the electrometer. By this means measurements could be obtained for liquids having a conductivity as high as 16×10^{-10} , or about 3400 times the highest conductivity in the former series. Calling K the sp. ind. cap., and k the conductivity, it was found that for distilled water $K = 76$, whilst k varied from 3.4×10^{-10} to 16×10^{-10} , so that an increase of conductivity to about five times its original value had no perceptible effect on the sp. ind. cap. For ethyl alcohol containing 2 per cent. of water, $K = 26.5$, and when, by the addition of traces of ammonium chloride, the conductivity was increased from 2.3×10^{-10} to 12×10^{-10} , the value of K remained sensibly constant. For amyl alcohol the values obtained were $K = 15$ and $k = 0.16 \times 10^{-10}$. When successive quantities of ethyl alcohol were added to pure xylene, both K and k increased, but the latter at first much more rapidly than the former, the change of k from less than 10^{-4} to 0.03 being accompanied only by a change of K from 2.36 to 3.08.

For these substances, Maxwell's law connecting sp. ind. cap.

and index of refraction does not hold even approximately, the deviation from the law being very much greater than even in the case of glass and the fatty oils. The author suggests that it would be of interest to investigate the sp. ind. caps. of aqueous and alcoholic solutions of various salts to as high a degree of concentration as possible, and also to determine the same constant for as many well-defined chemical compounds as possible, in order to see if it may not be possible to find some law connecting the sp. ind. cap. of a substance with its chemical constitution. G. W. T.

Conductivity and Specific Inductive Capacity. By E. COHN and L. ARONS (*Ann. Phys. Chem.* [2], **33**, 31—32).—In this note the authors state that the numbers 2·23 and 4·43 given by them in the paper referred to (*ibid.* [2], **28**, 454) as the specific inductive capacities of xylene and castor oil respectively are, according to their later researches, too small, and should be 2·36 and 4·82 respectively.

G. W. T.

Specific Inductive Capacity of Liquids. By F. TOMASZEWSKI (*Ann. Phys. Chem.* [2], **33**, 33—42).—The principal object of this investigation was to obtain measurements of the specific inductive capacities of certain liquids in order to determine, if possible, some relation between the value of this constant and the chemical constitution of the liquid, which curiously enough was one of the desiderata suggested by Cohn and Arons (preceding Abstracts).

There were two questions which presented themselves for solution : (1) The influence of the number of atoms in a molecule, requiring determinations for isomeric, homologous, and metamer compounds. (2) The effect of introducing a fresh element into the molecule, requiring determinations for non-homologous compounds.

The experiments were carried out by Silow's method slightly modified, and the charges were obtained from a battery of 40 zinc-copper-water cells.

The principal results obtained are given below, K being the specific inductive capacity, and μ the index of refraction for infinite wavelength.

Isomeric Compounds, C₁₀H₁₆.

	\sqrt{K} .	μ .
Oil of turpentine from <i>Pinus silvestris</i> , lævoro- tatory	1·5070	1·4689
Oil of turpentine from <i>Pinus maritima</i> , lævoro- tatory	1·5026	1·4561
Oil of turpentine from <i>Pinus Australis</i> , dex- trorotatory	1·5046	1·4685
Oil of citron	1·4990	1·4706

Homologous Compounds. Aromatic Hydrocarbons.

	\sqrt{K} .	μ .
Benzene (free from thiophen)	1.4892	1.4757
Toluene.	1.5175	1.4713
Paraxylene	1.5436	not determined.
Cumene	1.5627	1.4838

The specific inductive capacities of isomeric compounds are, therefore, not equal.

Where M is the molecular weight and d the density, it was found that the quantity $M(n-1)/d$, or the molecular refraction, was sensibly constant for the isomeric series, as also were the quantities $M(K-1)/d$ and $M(\sqrt{K}-1)/d$. The specific inductive capacity of homologous compounds is seen from the second table to increase with the number of atoms. Maxwell's relation $d = \sqrt{K}$ is only approximately true, as is clear from the tables given. G. W. T.

Electric Discharge through Gases. By A. SCHUSTER (*Proc. Roy. Soc.*, 42, 371-379).—A glass vessel is divided into two compartments by means of a metal plate nearly reaching to the sides and connected to earth. In one compartment charged gold leaves were placed, in the other electrodes through which discharges were passed from an induction coil. No effect was observed at the atmospheric pressure, but at 43 mm. pressure the leaves slowly collapsed. In another experiment, sparks from a Voss machine were passed at the atmospheric pressure between points or spheres in the neighbourhood of charged balls. When the electrodes were similar, whether points or spheres, the balls collapsed when electrified positively, but when one electrode is a sphere and the other a point, the balls collapse if their electrification is of opposite sign to that of the point. Finally, the author observes that in a partial vacuum incompletely divided into two compartments by a metal screen connected to earth, a continuous discharge between electrodes in one compartment renders it possible to send a current between electrodes in the other compartment with an indefinitely small electromotive force. In one case, a current of 0.008 ampère through the main electrodes enabled an E.M.F. of one-fourth volt to send a current through the auxiliary electrodes. The intensity of the auxiliary current is greater the greater the main discharge and the reduction of pressure; it increases less rapidly than the electromotive force causing it. Anything which facilitates gaseous diffusion increases the strength of the auxiliary current.

In explanation of these facts, the author considers that the two atoms of a gas molecule are charged with opposite electricities, and are held together by molecular forces. When this union is ruptured by the main discharge, the atoms diffuse across to the auxiliary electrodes, and give up their electricities to them. The rupture of the molecule is supposed to take place at the negative pole. The diurnal

variations of terrestrial magnetism are supposed to be due to currents produced by tidal or other regular motions, such feeble currents being rendered possible by the more powerful discharges which take place in the upper regions of the atmosphere.

H. K. T.

Conduction of Electricity through Gases. By F. NARR (*Ann. Phys. Chem.* [2], **33**, 295—301).—Hittorf (*Ann. Phys. Chem.*, **7**, 595) found that a pair of gold leaves attached to a stick of shellac, enclosed in a tube of hydrogen containing phosphoric acid to ensure perfect dryness, retained their charge after the lapse of four days, from which he concluded that dry hydrogen does not conduct electricity. Nahrwold (*ibid.*, **5**, 460), by a different method of experimenting, came to the conclusion that the particles of a gas cannot receive an electrostatic charge, and that the loss of charge of a conductor exposed to the air is due entirely to the presence of floating particles of dust. The author considers that Nahrwold's experiments only show that dust is the chief factor in causing leakage in a conductor exposed to the air.

He refers to some former experiments (*ibid.* [2], **5**, 145; **8**, 266; **11**, 155; **16**, 558; **22**, 550) made by him with a charged sphere suspended within an insulated conducting envelope containing different gases of various densities, carefully freed from dust. Whilst he confirmed Hittorf's result as to the charge being retained for a long time, he found that there is an instantaneous small loss of charge, depending on the nature of the gas and on its density. This instantaneous loss increases as the density is diminished, and a further instantaneous loss takes place when the envelope is connected to the earth, followed by a gradual and continuous loss of charge. The author attributes this sudden loss to a transference of electricity to the gaseous molecules, and the slow dispersion to an electrical connection between the sphere and the envelope. He has now repeated the experiments with a double metallic envelope containing gas. The envelopes were in the form of cylinders open at one end, and closed at the other, the closed ends being hemispherical. The open ends were closed by a sheet of glass covered with lac varnish, and the cylinders were cemented to it with their axes coinciding. The author then found a similar increased loss on connecting the outer envelope with the earth, from which he concludes that the gas between the two cylinders acted as a conductor, putting the inner one in connection with the outer, and so with the earth. The instantaneous loss of charge was found to increase when the density of either the inner or the outer portion of gas was diminished, which agreed with the former results, but the slow dispersion of the charge appeared to be sensibly independent of the density of the gas, as would be expected to be the case if the dispersion takes place by a convection of electricity by the gaseous particles, owing to the enormous number in contact with the surface of the envelope at any moment.

G. W. T.

Electrical Conductivity of Solutions of Neutral Salts. By G. JÄGER (*Monatsh.*, **8**, 721—724).—The electrical conductivities of some salts of heavy metals have been measured in solutions con-

taining proportions varying from $\frac{1}{20}$ to $\frac{1}{1280}$ of the gram-molecular weights per litre. The salts thus examined were lead nitrate and acetate; silver nitrate, sulphate, and acetate; zinc sulphate, bromide, and iodide, and copper sulphate and acetate. Dividing the observed conductivity by the proportion of the molecular weight in each case, the relative conductivity of the molecular weight of the salt for different dilutions is obtained. This plotted against the dilution values gives curves approximating to straight lines, although in no case could the conductivity be represented as of the form $L = \alpha m + \beta m^2$. All the curves, with the exception of that for zinc bromide, appear to tend towards maxima in different directions; this is taken as supporting the view that each salt has its own definite molecular conductivity.

H. C.

Comparative Properties of the Electrical Conductivities of Salt Solutions. By G. JÄGER (*Monatsh.*, 8, 725—733).—In a former paper (this vol., p. 217), the author proved that if L and L_1 are the molecular conductivities of two different salt solutions, δ the diameter of the molecule of the solvent, and d, d', d_1, d'_1 , those of the ions,
$$\frac{L}{L_1} = \frac{1/(d + \delta)^2 + 1/(d' + \delta)^2}{1/(d_1 + \delta)^2 + 1/(d'_1 + \delta)^2}$$
 From this it follows that as δ is increased, the value of L/L_1 will more nearly approximate to unity, or that as the size of the molecules of the solvent increase all molecular conductivities approach more nearly to the same value. A rise of temperature increasing the sphere of action of the molecule in accordance with the coefficient of expansion of the liquid, where this last is small and only small changes of temperature are dealt with, δ may be looked on as constant, and the above ratio as independent of temperature.

To test the above, a determination was made of the conductivities of solutions of sodium and potassium chlorides containing $\frac{1}{4}$ to $\frac{1}{32}$ gram-equivalent per litre in water, and in water containing 20 to 60 per cent. alcohol, glycerol, and sugar, in each of which cases the conductivity of the solvent may be neglected. Dividing the molecular conductivity of potassium chloride by that of sodium chloride in each case, it was found, as was expected, that water gave the highest values for the ratio, and that in the other cases the ratio decreased and approximated more to unity as the quantity of dissolved alcohol, glycerol, or sugar increased, or, as may be assumed, the diameter of the molecule of the solvent increased. That temperature would have no effect on the value of the ratio may be taken as proved by the result of Kohlrausch's experiments, "that the resistances of the ions in water are all altered in the same proportion by change of temperature."

Also, as a consequence of Kohlrausch's theory, $L/L_1 = (u + v)/(u_1 + v_1)$ where u, v, u_1 , and v_1 are the molecular velocities of the ions, it follows that if two salts have one ion in common, say, $u = u_1$, then L/L_1 approximates to unity as u increases, or the greater the molecular conductivities of two salts containing a common ion, the less will the ratio of the two conductivities differ from unity. This is also found to hold good when tested by the results of Kohlrausch's own experiments.

H. C.

The Electrical Conductivity of Solutions of some Fatty Acids in Water and in Alcohols. By K. HARTWIG (*Ann. Phys. Chem.* [2], **33**, 58—80).—The author points out that comparatively few investigations have been made into the conductivity of other than aqueous solutions. Of those known to the author, Mateucci (*Ann. Chim. Phys.*, **66**, 237) was the first who made experiments on alcoholic solutions, but Wiedemann has thrown doubt upon his conclusion that aqueous and alcoholic solutions of the same substance of the same specific weight conduct equally well. Oberbeck (*Ann. Phys. Chem.*, **155**, 595) measured the resistances of aqueous and alcoholic solutions of cadmium bromide and cupric chloride, and found that the conductivity was increased by each of these salts in a manner dependent on the salt and on the solvent. Guglielmo (*Atti R. Accad. Torino*, **17**) determined the conductivity of an alcoholic solution of potassium hydroxide, that of the aqueous solution having been previously determined by F. Kohlrausch. Vincentini (*Mem. R. Accad. Torino* [2], **36**, 22) investigated the conductivity of alcoholic solutions of some chlorides, and found that there is no simple relation between the solubility and the conductivity. Bartoli (*l'Orosi*, **7**, 3) showed that paraffin and naphthalene can be made into conductors by the addition of amyl alcohol and phenol. The same author (*R. Acad. Lincei*, **1**, 550) investigated the conductivity of various mixtures of organic compounds; and Lenz (*Mem. Ac. Sci. St. Pétersbourg*, **7**, 30) made some researches in the conductivity of aqueous and alcoholic solutions, in the course of which he completely demonstrated the falseness of Mateucci's conclusions. The author selected the fatty acids for his experiments, as being very soluble in several media.

The measurements were made by the Wheatstone bridge method, with a telephone as indicator. The substances experimented on were solutions of formic, acetic, and butyric acids in water, and in methyl, ethyl, and amyl alcohols. The measurements were made immediately after the solutions were made, and as none of them occupied more than an hour, it was found that the results were not sensibly affected by the etherification which always takes place when organic acids and alcohols are mixed.

With the exception of two of the solutions of formic acid, the author finds that the conductivity reaches a maximum at a certain concentration, and that this maximum is reached the sooner the worse the conductivity of the acid.

The table below gives the percentage of acid for which each solution has the maximum conductivity:—

Solution.	Acids.		
	Formic acid.	Acetic acid.	Butyric acid.
Water	30	16·6	12·0
Methyl alcohol	100	30·0	17·3
Ethyl alcohol	100	49·0	21·6
Amyl alcohol	—	54·0	26·0

Thus the greater the quantity of carbon present in the acid the sooner is the maximum conductivity attained, and the greater the quantity of carbon present in the solvent the later is the maximum attained, the conductivity being diminished by an increase of the quantity of carbon present either in the acid or in the solvent.

The author attributes the anomalous behaviour of formic acid with regard to electrical conductivity, together with similar anomalies which it exhibits with respect to its other physical properties, to the absence of the group methyl from its composition. G. W. T.

Electric Leakage. By J. J. THOMSON and H. F. NEWALL (*Proc. Roy. Soc.*, **42**, 410—429).—The liquid experimented on is contained in a cylindrical, metallic vessel, connected to earth, in which a metal cylinder is suspended by means of a silk thread; this can be connected either with a battery or with a quadrant electrometer. The inner cylinder, after being charged, is connected with the electrometer, and readings taken every five seconds. Curves are plotted showing (1) the decrease of potential with time; (2) the ratios of successive potential values. The liquids examined were benzene, olive oil, carbon bisulphide and paraffin oil, and were filtered many times before use. With the first three, no deviation from Ohm's law could be detected. With paraffin oil, the conductivity is slightly greater with large than with small differences of potential. These results, where the E.M.F.'s were 20—100 volts, differ from those of Quincke (*Abstr.*, 1886, 959), who finds that with E.M.F.'s sufficient to produce a spark the conduction does not even approximate to Ohm's law. With carbon bisulphide, great discrepancies were found in the first results; these were traced to differences in time of charging, and later experiments proved that electric absorption took place. The effect was greatest after redistilling the carbon bisulphide, but at times it was totally absent. The conductivity of all the liquids was increased by rise of temperature, so that in this respect they resemble electrolytes. H. K. T.

The Influence of Magnetic Forces on the Nature of the Heat Conductivity of Bismuth. By A. v. ETTINGSHAUSEN (*Ann. Phys. Chem.* [2], **33**, 129—136).—The author points out that Righi (*Abstr.*, 1887, 1009) and Leduc (*Compt. rend.*, **104**, 1783; **105**, 250) have made some experiments, from which they conclude that the thermal conductivity of bismuth in a magnetic field is diminished to an equal extent with the electrical conductivity, supposing the magnetic lines of force to cut the stream lines for heat or electricity respectively at right angles. Nernst (*Ann. Phys. Chem.* [2], **31**, 760) was unable to detect any change in the thermal conductivity. The author, after some experiments made with great care, finds that the thermal conductivity is diminished, but to a much less degree than the electrical conductivity. The decrease in the thermal conductivity is greater when the bismuth is impure, but still much less than that of the electrical conductivity. G. W. T.

Constancy of the Heat Produced by the Reaction of Silver Nitrate with Solutions of Metallic Chlorides. By T. W.

RICHARDS (*Chem. News*, 57, 16—17).—In these experiments, all necessary precautions are observed to obtain comparable conditions: 250 c.c. of the silver nitrate solution (equal to 4 grams silver nitrate) and 250 c.c. of the salt solution (containing a gram or so of the salt in excess of that required to precipitate all the silver) are poured simultaneously into the platinum calorimeter (Berthelot's), and the rise in temperature noted. The average rise in 20 experiments amounts to 16.165 cal. and all the results are practically identical; the experiments included sodium, potassium, ammonium, barium, cupric, zinc, manganous, nickelous, ferrous, aluminic, ferric, and chromic chlorides and hydrochloric acid. Taking the following equation as representing the reaction, the author concludes from these results that the amount of heat is constant no matter what R or n may be.
$$\left(\frac{1}{n}R_mCl_n + AgNO_3 + Aq\right) = AgCl + \left[\frac{1}{2}R_m(NO_3)_n = Aq\right].$$
 (Compare Pickering, this vol. p. 333.) D. A. L.

Relation between the Heats of Formation of Chlorides and Sulphates in Aqueous Solution. By I. W. FAX (*Chem. News*, 57, 36—37).—The author conducted a series of experiments with barium chloride and soluble sulphates exactly similar to Richard's experiments with silver nitrate and chlorides (see preceding Abstract). There is not that general regularity observed in the case of the sulphates as with the nitrates, although the rise for allied bases is quite close; the sesquioxide salts give a greater rise of temperature than the protoxide salts do, and with the double salts a still larger quantity of heat is evolved, whilst sulphuric acid gives most of all. The sulphates included in the experiments were sodium, potassium, ammonium, magnesium, zinc, cadmium, copper, nickel, cobalt, ferrous and ferric, and aluminium potassium alum, potassium chrome-alum, ammonium ferrous sulphate, and sulphuric acid. The results are tabulated in the original paper. (Compare Pickering, this vol., p. 333.)

D. A. L.

Alteration in the Volumes and Density of Liquids by the Absorption of Gases. By K. ÅNGSTRÖM (*Ann. Phys. Chem.* [2], 33, 223—233).—The author has already given an account of investigations on expansion of water through the absorption of gases (Abstr., 1882, 687). Since this appeared, experiments of the same nature have been made both for water and ethyl alcohol, by Blümcke (Abstr., 1885, 215; 1887, 435), but they do not agree with those made by the author or by Mackenzie and Nichols (Abstr., 1878, 366) and Nichols and Wheeler (*Phil. Mag.*, 5, 11, 113), probably because Blümcke's method did not allow of several requisite corrections being made; for example, for the compression of the areometer, and for the refraction of light at the surface of the containing vessel.

A summary of the results of the author's previous experiments and of the first series described in the present paper are given in the table below, in which δ_1 , δ_2 , δ_3 , are coefficients of expansion due to absorption.

	Carbonic acid δ_1 .	Air δ_2 .	Hydrogen δ_3 .	$\frac{\delta_1}{\delta_3}$.	$\frac{\delta_2}{\delta_3}$.
Chloroform	0·00188	0·00205	0·00160	1·18	1·28
Nitrobenzene	0·00168	—	—	—	—
Water	0·00130	0·00143	0·00106	1·23	1·35
Benzene	0·00200	0·00216	0·00170	1·18	1·27
Methyl alcohol	0·00184	0·00201	0·00157	1·17	1·28
Ethyl alcohol	0·00185	0·00203	0·00152	1·22	1·34
Ether	0·00200	0·00240	0·00184	(1·09)	1·30
			Means =	1·20	1·30

This shows that, except for ether, the ratios δ_1/δ_3 and δ_2/δ_3 are sensibly constant. Experiments on the successive absorption of two or more gases gave the result that the coefficient of expansion due to absorption is independent of any previous absorption of gas, the total expansion being equal to the sum of the expansions due to the absorption of the different gases.

The results obtained enable the change in the specific weight of a liquid due to the absorption of gas to be calculated, which is of practical importance for specific weight determinations, but the effect in such cases is so small that it need only be taken into account when the most extreme accuracy is desired. The author considers the constancy of the ratios δ_1/δ_3 and δ_2/δ_3 to be the most important of his results from a theoretical point of view, as it shows that the dilatation depends on the gas, and that the relations between the coefficients of dilatation due to absorption are independent of the nature of the liquid; from this he concludes that Ostwald's hypothesis (*Stöchiometrie*, p. 356), founded on the values of the coefficient of dilatation due to absorption obtained by the author and by Sarrau, namely, that "the volume of the absorbed gas is almost exactly reduced to the volume of its molecules," is *à priori* extremely improbable.

G. W. T.

Differential Tonometer. By G. J. W. BREMER (*Rec. Trav. Chim.*, 6, 122—136).—An apparatus for measuring the difference between the vapour-tension of a saline solution and the vapour-tension of water by allowing the vapours to act on the opposite ends of a column of olive oil. It consists essentially of small flasks connected with vertical tubes about 150 mm. high communicating with one another by means of a horizontal tube at the bottom. The particular apparatus described consists of four such flasks. The flasks should have exactly the same cubical contents, which may be adjusted by introducing pieces of glass rod, and should contain equal volumes of the solutions. After introduction of the liquids the flasks are cooled to 0°, rendered partially vacuous, and oil allowed to enter from the bottom horizontal tube until it rises to about half the height of the vertical tube. The exact pressure of the air in the flasks is observed, and the flasks and their contents are heated to different

temperatures and the differences between the levels of the oil in the tubes are observed.

Determinations of the vapour-tensions of aqueous solutions of calcium chloride of different strengths show that if the salt is regarded as existing in the liquid in the anhydrous condition, the reduction of the vapour-tension increases more rapidly than the amount of calcium chloride present, but if the solution is supposed to contain the hydrate $\text{CaCl}_2 + 6\text{H}_2\text{O}$, the reduction of the vapour-tension is proportional to the amount of salt present, as Wullner has previously stated.

C. H. B.

Dynamical Method of Determining Vapour-pressure. By G. TAMMANN (*Ann. Phys. Chem.* [2], 33, 322—337).—The author on recalculating some tables given by Regnault (*Ann. Chim. Phys.* [3], 15, 158) for the vapour-pressure of pure water determined by the dynamical and statical methods respectively, found that the close agreement of the results was only apparent, and that there were really some considerable discrepancies which could not be accounted for. The author now describes a number of experiments carried out principally with a view to testing the dynamical method, following Regnault with some modifications in details. He concludes that the method is not capable of giving good results. In the case of unsaturated solutions, when the current of air is passed over the surface of the solution, the upper layers become more concentrated than the lower, through the evaporation being entirely superficial, and if the current of air is led through the solution errors are introduced, as it is impossible to prevent variation of pressure and the scattering of drops of the solution upon the interior of the glass vessels. The author attempted to use it with saturated solutions, using filter-paper soaked in the solution, then partly dried, and introduced into a U-tube through which the current of dry air was allowed to pass, but then he was met by the difficulty that on taking the tube out of the bath used to maintain the required temperature, drops of water condensed on the inner surface of the tube, and dissolving some of the salt adhering to it gave rise to unsaturated solutions. The author next tried the method with hydrated salts in crystals. Here, however, the results were found to depend on the velocity of the stream of air, which appeared to be due to the water-vapour given off dissolving a portion of the crystals and forming hydrates containing less water, which would give a lower vapour-pressure.

From some of the results obtained during the last series of experiments, combined with Pape's result (*Ann. Phys. Chem.*, 124, 329) that rates of evaporation from the different surfaces of irregular crystals are not the same, the author draws the conclusion that the vapour-pressure at the surface of a crystal is not the maximum value of vapour-pressure due to the crystal. The vapour-pressure at the surface depends on the nature of the surface, and is considerably less when the surface is uninjured than when it is broken or otherwise changed.

G. W. T.

Compressibility of Rock Salt. By F. BRAUN (*Ann. Phys. Chem.* [2], 33, 239—240).—The author in a recent note (this vol., p. 214), whilst giving the preference to Röntgen and Schneider's value 5×10^{-6} for the cubic compressibility of rock salt over the value 1.4×10^{-6} found by him, as his own determination was a comparatively rough one, pointed out that according to Voigt's measurements of elasticity the value would be 1.6×10^{-6} . The author has since seen a later paper by Voigt (*Ann. Phys. Chem.* [2], 15, 497) in which he corrects his former result, as in obtaining it he made use of a torsion formula which he has since found to be incorrect. Voigt's later measurements would give the value 4.2×10^{-6} , which, considering the difficulty of the piëzometer method, agrees fairly with that obtained by Röntgen and Schneider. G. W. T.

Rate of Transformation of Metaphosphoric Acid. By P. SABATIER (*Compt. rend.*, 106, 63—66).—The conversion of metaphosphoric acid into orthophosphoric acid involves the introduction of an acid function of medium activity and an acid function of feeble activity, in addition to the original energetic function. Only the latter affects methyl-orange; the second feeble function affects phenolphthaleïn, the third can only be qualitatively recognized by means of the blue C4B. The acidity of the liquid h to methyl-orange remains constant, whilst its acidity to phenolphthaleïn ϕ increases, and affords a measure of the progress of the transformation. When conversion into orthophosphoric acid is complete $\phi = 2h$, and at any stage of the change $2h - \phi$ gives the amount of metaphosphoric acid y still remaining unaltered.

The metaphosphoric acid was obtained by dissolving phosphoric anhydride gradually in cold water, and also by strongly heating the ortho-acid, and dissolving the residue in water. Both preparations behaved in the same manner.

These solutions were heated at different temperatures for definite intervals of time. At a given temperature, $\log y$ is proportional to the time. The velocity of the change at each instant is proportional to the mass of transformable substance present in the system, and hence $\log y = -x \log a + \log b$, and therefore $y = ba^{-x}$, where b is the value of y at the commencement, and a is a constant which is a function of the temperature and the concentration, and increases with both, but the exact law of increase has still to be determined.

C. H. B.

Point of Transition and Point of Fusion. By J. H. VAN'T HOFF (*Rec. Trav. Chem.*, 6, 36—42; 91—94; 137—139).—The particular reaction considered is the conversion of mixtures of sodium and magnesium sulphates into astrakanite, $\text{Na}_2\text{Mg}(\text{SO}_4)_2 + 4\text{H}_2\text{O}$, at temperatures below 21.6° . It is found that in order to separate sodium sulphate from the mother-liquors from sea-water, which contain a large proportion of magnesium chloride, it is necessary to cool the liquid below 5° , and hence it would appear that the system $\text{MgCl}_2 + \text{Na}_2\text{SO}_4$ is stable below 5° , but at higher temperatures the reciprocal system is formed.

If a solution containing sodium sulphate and magnesium chloride

in equivalent proportions is placed in a dilatometer, no anomalous expansion is observed at 5° , but if 2 mols. of sodium sulphate are present for each molecule of the magnesium salt, there is a very considerable expansion if the liquid is heated above 5° , and a considerable contraction if it is cooled below this temperature. This particular temperature is in fact the point of transition between the two systems, but the author has previously observed that magnesium chloride cannot exist in presence of sodium sulphate at temperatures below 5° , because the tension of the water of crystallisation of the latter salt is less than the vapour-tension of the saturated solution of the two salts.

The slow evaporation at a low temperature of a solution containing sodium chloride and sodium and magnesium sulphates in equivalent proportions yields a mixture of the three salts, but if evaporation takes place at a higher temperature cubical crystals of sodium chloride are obtained, together with rosettes of astrakanite, which is formed by the union of the two sulphates with elimination of water. In presence of sodium chloride, formation of astrakanite takes place at 6° , and the reverse change at lower temperatures, whilst in absence of sodium chloride astrakanite is formed at 21.6° (Alstr., 1886, 968). The reduction of the point of transition from 21.6° to 5° by the presence of sodium chloride, corresponds with the reduction which this salt produces in the freezing point of its solution.

The double acetate, $\text{CuCa}(\text{C}_2\text{H}_3\text{O}_2)_4 + 8\text{H}_2\text{O}$, decomposes at 75° into the simple salts $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{H}_2\text{O}$ and $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{H}_2\text{O}$, with elimination of 6 mols. H_2O , and the change is accompanied by a distinct contraction; at lower temperatures, the double salt is formed, and expansion takes place. The volume changes are analogous to those which accompany the solidification of water, and it was to be expected that the effect of pressure would be analogous in the two cases.

At the author's request, Spring has subjected the double acetate to high pressures at varying temperatures, and finds that under a pressure of 6000 atmospheres decomposition takes place at 40° . Under the same pressure at 16° , there is no appreciable decomposition if the duration of the experiment is short, but if pressure is prolonged, evidence of decomposition is readily recognisable. Under a pressure of 2000 atmospheres, decomposition takes place distinctly at 50° (compare this vol., p. 341).

Van't Hoff points out that determinations of the minimum pressure required to produce reactions of this kind, together with measurements of the resulting changes in volume, will make it possible to express in kilogram-metres the absorption of energy involved in the reaction, and conversely the liberation of energy resulting from the reverse change.

C. H. B.

The Position of Atoms in Space. By J. WISLICENUS (*Ber.*, 21, 581—585).—Lössen has challenged Van't Hoff and Wislicenus to state their views on units of affinity from the standpoint of their geometric theory, and he affirms that the question of the position of the units of affinity in space must be answered not after, but before,

the question of the positions of atoms in space, and above all that a definition of "unit of affinity" must be given (this vol., p. 218).

The author admits that his views quite bar the conclusion that atoms are material points, and it is impossible, therefore, to consider them as configurations in space in which the several chemical units of action of polyvalent elements can be localised. But this conclusion is admissible when the so-called atoms are considered, not as atoms in the strict sense of the word, but as simple groups of primitive atoms, similar to the compound radicles but less complex; and therefore the position of the elementary atoms in the molecule must be determined before Lössen's demand can be taken into earnest consideration.

The author has shown that the determination of the arrangement in space of the atoms in a molecule is within the domain of experiment, and he points out that the study of the configuration of the molecule is the only way to solve successfully the question of the distribution in space of its spheres of action—the so-called units of affinity. Only by studying the properties of molecules can inductive conclusions be drawn as to the properties of atoms.

The author's views are stated as follows:—It is more probable that the atoms are configurations in space composed of atoms of primitive elements than that they are simply points of energy; the most likely assumption is, therefore, that the atoms are comparable with the compound radicles, and, as in the latter, their units of affinity are located in certain parts from which they exercise their action.

It is possible, in time, to succeed in obtaining definite ideas not only of the form of elementary atoms, but also of the relative positions of their spheres of action.

It is not impossible that the atom of carbon resembles more or less in form a regular tetrahedron, and that the causes of those actions, which are evidenced by the units of affinity, are concentrated in the angles of this tetrahedric configuration, perhaps for analogous reasons, and similarly to the electric action of a charged metallic tetrahedron. The real carriers of energy would finally be the primitive atoms, exactly as the chemical energy of compound radicles is the resultant of the energy of the elementary atoms.

F. S. K.

The Atomic Weights of the Elements. By A. BAZAROFF (*J. Russ. Chem. Soc.*, 1887, 61—73).—The author finds that the variation in the numbers expressing the atomic weights of the elements, arranged according to the periodic system, is analogous to the changes in the properties of the elements and their compounds. When the most probable numbers for the atomic weights of the elements are arranged according to the periodic law, and, either in the horizontal or in the vertical series, the atomic weight of an element is divided by the atomic weight of the element with the next lower atomic weight, products are obtained which decrease regularly with increase in the atomic weights compared. In the horizontal series, the maximum is found to correspond with the relation of $\frac{\text{Be}}{\text{Li}} = \frac{9.08}{7.01} = 1.2953$, the

minimum to $\frac{\text{Bi}}{\text{Pb}} = \frac{207.5}{206.39} = 1.0054$. This decrease, however, is not

continuous, the products alternately decreasing and increasing, as is seen from the following examples:—

$$\frac{\text{Mg}}{\text{Na}} = 1.0411, \quad \frac{\text{Al}}{\text{Mg}} = 1.1295, \quad \frac{\text{Si}}{\text{Al}} = 1.0355, \quad \frac{\text{P}}{\text{Si}} = 1.1057, \\ \frac{\text{S}}{\text{P}} = 1.0329, \quad \frac{\text{Cl}}{\text{S}} = 1.1060, \text{ \&c.}$$

This relation is best represented graphically, the order of atomic weights standing as abscissæ, and the aforesaid quotients as ordinates: in this way a curve of zigzag form is obtained. This relation is expressed by the author in the form of a law, namely, that “the increase in the atomic weights of the elements proceeds with a variable intensity, the smaller coefficient of change varying with the larger in such a way that both regularly decrease.”

Another regularity is observed in the vertical groups, for example, with the coefficients in the second group:—

$$\frac{\text{Mg}}{\text{Be}} = 2.6366, \quad \frac{\text{Ca}}{\text{Mg}} = 1.6671, \quad \frac{\text{Zn}}{\text{Ca}} = 1.6257, \quad \frac{\text{Sr}}{\text{Zn}} = 1.3456, \\ \frac{\text{Cd}}{\text{Sr}} = 1.2795, \quad \frac{\text{Ba}}{\text{Cd}} = 1.2252.$$

This change the author expresses by the law: “In the vertical series in the periodic system, the relation of two neighbouring atomic weights decreases with increasing atomic weight, but this decrease is alternately larger and smaller.” Neither of these functions extends to the whole periodic system, as there are many elements whose atomic weights are not yet determined with sufficient accuracy. Yet it is possible, from the data which are to hand, to state the following general law: “The magnitude of the atomic weight of each element is determined by the magnitude of the atomic weights of the elements next to it in the periodic system both horizontally and vertically.”

The author further analyses the exceptions to the said rules, and expresses the opinion that several of them are due to the atomic weights not being determined with sufficient accuracy, but it is difficult to say how far he is right in correcting several of the better determined numbers (he assumes for Tl 202 instead of 203.7!). Notwithstanding the apparently complicated character of the relation pointed out, the author thinks it possible that when the fundamental data are more exactly determined, it may be possible to calculate the atomic weight of an element with greater accuracy than is the case at present.

B. B.

Raoult's Method of Determining Molecular Weights.* By V. MEYER (*Ber.*, 21, 536—539). In investigating some derivatives of benzil, two series of isomeric compounds were obtained; both series have the same constitution, in the ordinary sense of the word, and are yet distinct from one another and yield different derivatives. The

* Raoult's papers on this method are *Abstr.*, 1883, 7, 278, 952; 1884, 254, 701, 808, 952, 1248; 1885, 122, 858; 1886, 197, 763. Compare also this vol., p. 361.

isomerism of the two series is expressed by the formulæ

$$\begin{array}{c} \text{Ph}\cdot\text{C} : \text{R} \\ | \\ \text{Ph}\cdot\text{C} : \text{R} \end{array}$$

and

$$\begin{array}{c} \text{Ph}\cdot\text{C} : \text{R} \\ | \\ \text{R} : \text{C}\cdot\text{Ph} \end{array}$$

By means of a modification of Raoult's method for determining molecular weight by measuring the amount by which the solidifying point of a solvent is lowered by a known weight of a dissolved substance, it is shown that the molecular weight of the compounds of the two series in question is identical. The method employed, which only involves the use of an ordinary thermometer divided into 0.1° and a simple apparatus, will be described.

N. H. M.

Application in Chemical Laboratories of Raoult's Method for Determining Molecular Weights. By K. AUWERS (*Ber.*, 21, 701—719).—The use of Raoult's method for determining molecular weights by V. Meyer (preceding Abstract) led to a consideration of the conditions necessary for its successful application. The exception which many solutions, notably those of inorganic salts in water, show to the law put forward by Raoult (*Abstr.*, 1886, 763), renders this law useless for practical purposes, and the relation $M = T/A$, where M is the molecular weight, T the molecular depression, and A the depression caused by 1 gram of substance in 100 grams of solution, is used. It is recommended to first determine the value of T , which will be constant for the series of compounds under consideration, by taking members of the series of known molecular weight. A measurement of A then suffices to determine M in subsequent cases.

A great objection is the impossibility of working with relatively small amounts of material, for although the above relation does not hold for concentrated solutions, the solutions must not be too dilute, and some discrimination is necessary in adjusting the strength to give the depression which should be measured in each case. With regard to the solvents used, it is of course a condition that no chemical action should take place between the one selected and the substance under examination. The selection of a suitable solvent is a matter of great importance.

Water is generally objectionable on account of its tendency to form hydrates and its non-solvent action on most organic compounds. As it is necessary also, according to Raoult, that the depression measured should not be less than 0.5° , as the relation does not hold when it is allowed to sink below that value, a relatively large quantity of material is necessary for each determination. Benzene gives better results, but cannot be used in the case of alcohols, phenols, or acids, and introduces an element of uncertainty in dealing with substances allied to these.

By far the best solvent, and the one that can be used with the greatest range of substances, is glacial acetic acid. The errors in this case are small, and the measurement of a depression of about 0.3° suffices. A great advantage also is that this solvent admits of working at ordinary temperatures. It is, however, found necessary, owing to its

hygroscopic nature, to conduct the experiments in a closed space, and an apparatus has been devised and is described by means of which this is easily rendered possible. A thermometer divided to one-tenth of a degree was used, and this was found to give sufficiently accurate results. Experiments are detailed with naphthalene and picric acid, acetanilide and benzil, and the isomeric diacetyl-compounds of β -diphenylglyoxime.

In conclusion, the author recommends the use of Raoult's method in those cases where vapour-density determinations are not possible.

H. C.

Isonitroso-compounds. By E. BECKMANN (*Ber.*, 21, 766—769).—The application to the ketoximes of Raoult's method for the determination of the molecular weight by the lowering of the freezing point, has led to the important result that the molecular weights are twice as large as has hitherto been assumed. The compounds experimented with were acetoxime and camphoroxime; the solvent being benzene.

With benzaldoxime and anisaldoxime, results were obtained pointing to molecular weights about one and a half times as great as those previously adopted; these results are, however, doubtless due to partial dissociation of the double molecule.

A. J. G.

Desiccation of Gases. By J. D. VAN DER PLAATS (*Rec. Trav. Chim.*, 6, 45—59).—An extended historical summary of the various methods which have been proposed for the desiccation of gases, together with an account of experiments made by the author. Anhydrous calcium chloride is more efficient than calcium chloride containing 2 mols. H_2O , but the difference diminishes at low temperatures. Calcium oxide absorbs moisture more slowly than anhydrous calcium chloride, and leaves twice as much water in the air as calcium chloride containing 2 mols. H_2O . Fused potash acts rapidly and much more completely than anhydrous calcium chloride, but less rapidly and less completely than concentrated sulphuric acid. Potash solution of sp. gr. 1.25 loses a considerable quantity of water if a current of air is passed through it for some time.

Ammonia is almost completely dried by fused potash.

Calcium chloride is a convenient but not very efficient desiccating agent. If the solution has been evaporated at 180° , it always contains calcium oxide, which cannot be neutralised even by the prolonged action of carbonic anhydride or hydrogen chloride so long as the salt remains dry.

Phosphoric anhydride is the best of all desiccating agents at present known, but it is inconveniently light and bulky. Not unfrequently it contains phosphorous anhydride, but this can be removed by Stas's method of distilling it in dry air.

Concentrated sulphuric acid is cheap and convenient, allows the speed of the gaseous current to be watched, and dries gases almost perfectly. It gives off no vapours, and when cooled its efficiency is increased. It must not contain sulphuric anhydride, and the presence of 6 to 8 per cent. of water is desirable in order to ensure absence of the anhydride in the gas which is passed through the acid. Some-

times the acid contains sulphurous anhydride, but this is readily removed by a current of dry air or by boiling the acid. Sulphuric acid will dissolve carbonic anhydride, but this gas is removed in a few minutes by passing a current of air into the liquid. The distribution of sulphuric acid with a view to expose a large surface is best effected by means of broken glass. Pumice should be boiled with sulphuric acid containing a little nitric acid in order to remove chlorides and fluorides and metallic oxides which might absorb oxygen. Sulphuric acid, especially if cooled, is practically as efficient as phosphoric anhydride, and the errors due to its employment are certainly not greater than those arising from the use of india-rubber connections or from neglect to remove, by heating, the layer of moist gas condensed on the surfaces of the glass vessels.

India-rubber cannot be completely dried on a sand-bath, but should be kept over sulphuric acid in the dark for a long time. Tubing with walls 5 mm. thick allows air and aqueous vapour to pass extremely slowly, and its power of absorbing carbonic anhydride is at a minimum.

Drying tubes, &c., which have to be weighed should be kept under a bell-jar containing vessels filled with the same desiccating agent as the tubes themselves contain.

C. H. B.

Delicate Thermometer for Lecture Purposes. By S. YOUNG (*Chem. News*, 56, 261).—For this purpose the author recommends an air thermometer of the form commonly employed to show the expansion of air with rise of temperature, but using a volatile liquid such as ether in place of mercury or sulphuric acid; to make the column of liquid visible at a distance, a little absolute alcohol coloured with aniline red is added. The apparatus employed by the author had the following dimensions: the cylinder at the bottom containing the air confined by ether was 17 mm. in diameter and 130 mm. long, the narrow tube extended 700 mm. above this cylinder and had a diameter of 2.8 mm., above this there was a reservoir large enough to hold the ether when the temperature got beyond the range of the thermometer. The total rise of column for 10° in the thermometer described was 510 mm.; for 1° between 0° and 1° the rise = 40 mm., whilst between 9° and 10° it = 82 mm.

D. A. L.

Lecture Experiment for Demonstrating the Valency of Metals. By B. LEPsius (*Ber.*, 21, 556—561).—The method which Nilson and Petterson have recently described for determining the atomic weights of the rare earths can be employed for demonstrating the valency of metals. A quantity of the pure metal, proportional to its atomic weight, is heated in gaseous hydrogen chloride, the volume of liberated hydrogen being proportional to the valency of the metal. For various reasons many of the metals offer great difficulties in carrying out this experiment, and the author recommends thallium, zinc, and aluminium as the most suitable examples. The hydrogen chloride, which must be perfectly dry, is obtained by acting on solid sublimed ammonium chloride with concentrated sulphuric acid in a Norblad's apparatus; it is passed through a combustion tube which contains weighed portions of the above-named metals (twice the

atomic weight) placed at intervals of 10 cm. from one another. The liberated hydrogen is collected in a graduated three-limbed glass apparatus filled with a 5 per cent. solution of potash and provided with a mercury seal. By heating the metals successively, the hydrogen evolved from each can be collected separately and the volumes compared directly.

F. S. K.

Inorganic Chemistry.

The Composition of Water by Volume. By A. SCOTT (*Proc. Roy. Soc.*, **42**, 396—400).—The ratio by volume in which oxygen and hydrogen combine at 0° and 760 mm. is redetermined. The apparatus is so arranged that both gases are measured in the same vessel, a separate vessel being used for exploding. After explosion, the residue was analysed by exploding with oxygen or hydrogen and the impurity (nitrogen and carbonic anhydride) determined. The oxygen was obtained from potassic chlorate and from mercuric oxide prepared from the nitrate, the hydrogen was obtained by electrolysis. The ratio obtained is 1.994:1, which with 15.9627 for the density of oxygen, gives 16.01 as the atomic weight of oxygen. H. K. T.

The Weldon-Pechiney Process for the Manufacture of Chlorine from Magnesium Chloride. By J. DEWAR (*J. Soc. Chem. Ind.*, **6**, 775—790).—This process, which was patented in June, 1884 (Eng. Pat. 9306), has recently been worked at Salindres on an experimental plant designed for the daily production of 1 ton of chlorine, and may be briefly described as follows:—The raw material employed is hydrochloric acid, the operations being (1) dissolving magnesium oxide in hydrochloric acid; (2) preparing magnesium oxychloride; (3) crushing, breaking, and sifting the oxychloride; (4) drying the oxychloride; and (5) decomposing the oxychloride. The magnesium oxide to be dissolved in hydrochloric acid is a portion of that which results from the fifth operation. The hydrochloric acid also results in part from the fifth operation and the remainder from the decomposition of salt. The solution obtained is evaporated down to the point at which it will contain not more than about six equivalents of water, and is then converted into oxychloride by mixing one equivalent of magnesium chloride with one and a third equivalents of magnesium oxide. This operation lasts only about 20 minutes, but during this time the whole mass becomes very hard and during solidification disengages much heat. The product is then in the form of solid pieces of different sizes along with a small quantity of powder. It is necessary to reduce this material to fragments, of which the largest shall not exceed the size of a walnut, and further to clear them of dust which might, when in the decomposing furnace, prevent free passage of air through the mass; this is effected by crushing it between cylinders bristling with diamond points, and

then passing it through a rotating sieve. The oxychloride is then dried, this operation being necessary, as in the decomposition a larger quantity of free chlorine and a smaller amount of hydrogen chloride are produced if the material contains less water, and the decomposition is performed at a higher temperature, both conditions being realised by drying previous to decomposition. The dried oxychloride is then decomposed in a special apparatus consisting of a series of furnaces provided with decomposing chambers heated by a movable regenerative burner, the oxychloride being decomposed in a current of air. The author's theory of the decomposition which goes on in the furnace is that in the first stage there is a rapid evolution of steam, the steam decomposing a portion of the magnesium chloride with formation of hydrogen chloride which passes off with the vapour of water. Anhydrous magnesium chloride and magnesium oxide remain, and this mixture then undergoes decomposition into magnesium oxide and chlorine by the action on it of atmospheric oxygen. The products are drawn off from the furnace by means of a diminished pressure steadily maintained, an aspirator being employed which acts through an ordinary hydrochloric acid condensing tower, a number of sand-stone bonbonnes and a glass tube refrigerator, the latter being in immediate connection with the decomposing furnace. The hydrochloric acid is condensed in these apparatus, whilst the mixture of air and chlorine passes on through the aspirator and is employed for the manufacture of chlorate: for this purpose, it is driven into special apparatus, wherein the chlorine acts on calcium hydroxide and gradually transforms it into a mixture of calcium chlorate and calcium chloride.

D. B.

Nitrogen Chloride. By L. GATTERMANN (*Ber.*, 21, 751—757).—The composition of nitrogen chloride has not yet been satisfactorily determined; weighed quantities of the chloride have never been analysed, but merely the ratio of nitrogen to chlorine determined in an unknown amount of the chloride, and, as is well known, the results obtained by different observers are by no means in accordance. In the present research, the experiments were carried on as far as possible in the glass case devised by V. Meyer (*Ber.*, 21, 26).

The nitrogen chloride was prepared in the usual manner by the action of chlorine on a solution of ammonium chloride. No sign of the formation of the chloride was visible until more than half the chlorine was absorbed, when the formation of minute drops was noticeable in the layer of liquid drawn up by capillary attraction on the sides of the flask; this soon spread and formed a thin film on the surface of the liquid, and this film in turn gradually separated into larger drops, the heavier of which sank, but were again brought to the surface by the nitrogen bubbles formed in the slight decomposition which goes on. When no more drops are formed, the chloride by careful shaking was made to fall into a small leaden capsule provided with a handle. It was then poured, with the aid of a funnel, into a thin-walled separating funnel, the ammonium chloride solution removed by a pipette, and the nitrogen chloride repeatedly washed by shaking with water until the washings no longer gave a chlorine reaction. To

assist the removal of dissolved chlorine from the oil, air was repeatedly blown through it by means of a glass tube, so that the oil was disseminated through the liquid in small drops. The successful carrying out of these operations shows that nitrogen chloride is by no means so readily exploded as has usually been supposed. The purified oil was next transferred to a thin glass flask (an operation attended with much danger owing to the friction of the stopcock of the separating funnel), dried by agitation with a small, clean piece of fused calcium chloride, and poured into the weighing glass—a weighed cylindrical vessel of about 1 c.c. capacity, provided with a stopper not quite airtight. The weighing was effected in the usual manner, save that a glass screen was again employed. The weighed substance was then decomposed by aqueous ammonia, and the chlorine estimated as silver chloride. The results showed that the product of the action of chlorine on ammonium chloride is invariably a mixture of several chlorinated ammonias, and that the product was richer in chlorine the longer the oil was in contact with chlorine, but under no conditions was the trichloride obtained directly.

After washing out the ammonium chloride as described above, the separating funnel containing the crude product covered with a few drops of water was placed horizontally, and a moderately strong stream of chlorine passed through for half an hour. The oil so obtained, after washing and drying, was analysed, and proved to be pure nitrogen trichloride.

Nitrogen chloride explodes on exposure to a strong light—either bright sunshine or magnesium light, although not so readily in the latter case. As in the author's experiments, no explosions occurred for which a cause could not be assigned, it seems very probable that the so-called spontaneous explosions experienced by other observers may be attributed to the action of light.

About $\frac{1}{2}$ gram of nitrogen chloride was heated in a thin-walled tube immersed in a beaker filled with liquid vaselin. Up to 90° no change was observed, but about 95° a violent explosion suddenly occurred. As has been noticed before in the explosion of nitrogen chloride, the main force of the explosion was exerted in a downward direction.

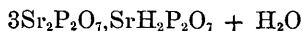
A. J. G.

Pyrophosphates. By G. v. KNORRE and E. OPPELT (*Ber.*, **21**, 769—773).—Pahl has stated (this *Journal*, 1875, 375, 774) that he obtained an acid calcium pyrophosphate by the action of oxalic acid on normal calcium pyrophosphate: although closely following his directions, the authors have failed to obtain any such salt, pyrophosphoric acid being formed, nor is any acid pyrophosphate formed by the action of pyrophosphoric acid on the normal salt.

By adding calcium chloride to a moderately concentrated solution of dihydrogen disodium pyrophosphate, a white, crystalline precipitate is obtained of the formula $2\text{CaH}_2\text{P}_2\text{O}_7, \text{Ca}_2\text{P}_2\text{O}_7 + 6\text{H}_2\text{O}$, this can be recrystallised from hot water in which it is very sparingly soluble. When this is boiled for a long time with hot water, it is decomposed, and the residue, after thorough washing, has the composition



From concentrated solutions of strontium chloride and dihydrogen sodium pyrophosphate, a slight flocculent precipitate of the composition $2\text{Sr}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{SrP}_2\text{O}_7 + 6\text{H}_2\text{O}$ is obtained; from dilute solutions, a crystalline precipitate separates of the formula $3\text{Sr}_2\text{P}_2\text{O}_7 \cdot \text{SrH}_2\text{P}_2\text{O}_7 + 2\text{H}_2\text{O}$, whilst if the solution is heated to boiling, the salt



is formed.

Solutions of barium chloride and dihydrogen sodium pyrophosphate when mixed in the cold yield the white crystalline salt



Action of Arsenious Trisulphide on Iodine. By R. SCHNEIDER (*J. pr. Chem.* [2], **36**, 498—515).—A solution of iodine in carbon bisulphide is without action on natural arsenious trisulphide (orpiment), but reacts with that precipitated by hydrogen sulphide, forming arsenious iodide and sulphur. Attempts to prepare the compound $\text{As}_2\text{S}_3 \cdot 2\text{AsI}_3$ by heating a mixture of iodine and arsenious trisulphide in the ratio $\text{As}_2\text{S}_3 : 6\text{I}$, were not successful. The mixture fused at a low temperature to a homogeneous mass of a brown colour, which dissolved almost entirely in carbon bisulphide; on evaporation of the solvent nothing but arsenious iodide and sulphur crystallised out. On distilling a mixture of arsenious trisulphide and iodine in the ratio $\text{As}_2\text{S}_3 : 6\text{I}$ until two-thirds of the material had passed over, the distillate was found to contain 58.63 per cent. of free iodine, 40 per cent. of arsenious iodide, and 1.37 per cent. of sulphur; the residue consisted of 55.32 per cent. of arsenious trisulphide and 44.04 per cent. of arsenious iodide. When in place of the former, a mixture of arsenious iodide and sulphur in the ratio of $2\text{AsI}_3 : 3\text{S}$ was employed, and the distillation continued until half the material had passed over, the distillate contained 69.44 per cent. of free iodine, 28 per cent. of arsenious iodide, and 2.56 per cent. of sulphur. These experiments show that whilst a mixture of arsenious trisulphide and iodine is converted at moderate temperatures into arsenious iodide and sulphur, these products again react at higher temperatures, reproducing their generators. If the distillate, rich in iodine, is sealed up in a glass tube, which is slightly inclined so that the distillate occupies the higher portion of the tube, and gently heated in a water-bath to a temperature of about 72° , a dark-brown liquid which solidifies on cooling trickles to the bottom of the tube. By repeated liquations in sealed tubes this dark-brown mass becomes perfectly homogeneous, crystallising in hard, brittle plates of a greyish-black colour, and dull lustre. The pure substance melts at 72° , and is represented by the formula $\text{SI}_6 \cdot 2\text{As}_2\text{I}_3$. On pulverising, it forms a reddish-brown powder which by exposure to the air rapidly loses iodine, whilst the residue, consisting of a mixture of arsenious iodide and sulphur, assumes a bright-red colour.

On fusing a mixture of arsenious trisulphide with iodine in the ratio $\text{As}_2\text{S}_3 : 4\text{I}$, the iodine reacts with only two-thirds of the arsenious trisulphide present. When, as not infrequently happens, the arsenious trisulphide contains arsenious acid, there remains behind, after fusion

with iodine and treatment with carbon bisulphide, an insoluble pale-yellow powder of the formula $2\text{As}_2\text{S}_3, 3(\text{AsI}_3, \text{As}_2\text{O}_3)$. This substance can also be prepared by heating a mixture of arsenious trisulphide (1 part) and arsenious iodide (0.2 part) with a large excess (8 to 10 parts) of arsenious iodide, or by heating a mixture of arsenious iodide (4 mols.) with arsenious trisulphide (1 mol.) with free access of air. Under the microscope, the compound appears to be indistinctly crystalline. On gently heating it, arsenious iodide first sublimes, then arsenious acid, and lastly arsenious trisulphide. The compound is completely dissolved by solutions of potash and ammonia, and is readily decomposed by the common mineral acids and by boiling water. G. T. M.

Silicon. By H. W. WARREN (*Chem. News*, **57**, 54).—The following is a new method of preparing silicon. Small bars of "silicon-eisen" are suspended in dilute sulphuric acid from the positive pole of a battery of two ferric chloride cells and are in contact with a platinum plate forming the negative pole. The iron dissolves and leaves a residue of graphite, silica, and amorphous silicon, which is heated to redness in a stream of carbonic anhydride, and then to a full red heat in a closed iron tube with some zinc; the zinc button obtained in this manner is dissolved in hydrochloric acid, when crystalline silicon remains undissolved; by heating the amorphous silicon at a full white heat with aluminium instead of zinc, graphitoid silicon is obtained. When an alloy of aluminium and silver is heated to an intense white heat with potassium silicofluoride, small quantities of silicon are produced in the form of a bright reddish-brown powder. D. A. L.

Silver Suboxide and the Action of Potassium Permanganate on Silver. By C. FRIEDHEIM (*Ber.*, **21**, 307—318).—The first part of this paper is devoted to a criticism of v. d. Pfordten's latest communication on this subject (this vol., p. 221), and, in particular, attention is drawn to the fact that he no longer insists that the substance in question is silver suboxide, but only that it is not metallic silver. Referring to the statement that silver is dissolved by water acidified with sulphuric acid and exposed to the air, the author again states that the metal could not be detected in the solutions at the end of each experiment (compare Abstr., 1887, 1079). The action of permanganate has been studied under new conditions in an apparatus so contrived that a solution of permanganate acidified with dilute sulphuric acid placed in one bulb could by means of a connecting tube be brought in contact with a silver mirror in a second bulb after the bulbs and contents had been heated at 50° and at 100° respectively for 4 to 5 hours, whilst the apparatus was connected to a Töpler-Hagen's mercury pump, and then allowed to cool. Various strengths of permanganate were used, and in one experiment spongy silver was employed, but the results in every case showed that the permanganate acted at once on the silver and completely dissolved it. Experiments with the acidified permanganate solution *per se* showed that, on boiling, a decomposition occurred with the separation of an ochre-yellow or black oxide of manganese according to the concentration of the

solution, and that this decomposition also occurred, although to a much smaller extent when the solution was heated at 40—50° for 4 to 5 hours in a vacuum. On this account, v. d. Pfordten's experiment of treating silver with a boiling acidified permanganate solution in a current of carbonic anhydride was not repeated, but in its stead the experiment in a vacuum was modified to the extent of filling the cold vacuous apparatus with pure carbonic anhydride (free from air) under pressure; connection was then made between the bulbs, with the result that the silver dissolved as before.

In reply to other objections to the author's views (*loc. cit.*) raised by v. d. Pfordten, it is pointed out that the complete dissolution of the latter's preparation (before ignition) in nitric acid does not disprove the presence of organic matter, since many organic substances are completely soluble in nitric acid. Again, the statement that no case is known in which impurity in the silver hinders amalgamation is met by an experiment in which an intimate mixture of finely divided silver and magnesia, obtained by adding calcined magnesia to a neutral solution of silver nitrate and igniting the precipitate, was shaken continuously with mercury for eight hours with the result that 1.149 gram of silver was dissolved and 0.8322 gram remained in the residue; hence v. d. Pfordten's argument, based on the fact that his substance underwent no change when shaken with mercury, is open to criticism. Finally, the change of colour from black to grey occurring when the so-called suboxide is treated with sulphuric acid or solutions of indifferent salts (*Ber.*, 20, 1470, 3379) is paralleled by a similar change under like conditions in the colour of metallic silver precipitated from an ammoniacal solution of silver chloride by zinc, or from neutral silver solutions by other metals (*Vogel, Ber. Berl. Akad.*, 1862, 289). On these grounds, and without contesting the question of the existence of silver suboxide, the author maintains that v. d. Pfordten's substance is not this compound, but a mixture of finely divided silver with more or less silver oxide or organic matter.

W. P. W.

Lead Slags. By M. W. ILES (*Chem. News*, 67, 4—7, 18—19, 37—38, 43—45, 57—58).—This communication contains the results obtained, and observations made in a very extensive investigation into the character and composition of lead slags. The sp. gr. of lead slags varies from 3.3 to 4.16, the best slags having a density of 3.4 to 3.65. Iron, barium, and lead cause high sp. gr.; aluminum, silica, and lime low gravities. All good slags are as a rule more or less perfectly crystalline; slow cooling favours crystallisation, sudden cooling impedes crystallisation or even stops it altogether, hence the crusts of pots of slag are devoid of crystalline structure. Well-crystallised slags have definite fusing points, and are more brittle than the imperfectly crystalline slags, and are only partially soluble in strong acids; the form of crystallisation serving as an important indication of the quality of a lead slag. Slags cooled by pouring into water are amorphous, have their fusing point lowered, resemble obsidian in appearance, and when pulverised are completely dissolved by hydrochloric acid. The author takes advantage of this property in taking and preparing samples for analysis; the crust of the pot of slag is thrown aside, a steel bar is

thrust about 2 inches deep into the molten slag and then plunged into water. The outside rims of pots of slag are subject to rapid cooling. The colour of lead slags is almost always black or a dark shade. Lustrous black and the darkest slags contain most iron, this element, however, sometimes imparts a reddish tint, sometimes a slight greenish cast; lime tends to lighten the colour, giving the slag a stony or earthy appearance; large quantities of manganese give a reddish to amethystine hue, and when associated with 20 per cent. or more of lime, the slag has very often a resinous colour. Zinc in the presence of alumina, manganese, and much silica produces a porcelain or obsidian-like slag, whilst some very siliceous slags have a greenish cast. The lustre of lead slags is rarely pearly, often resinous, submetallic splendent, and pitchy; most are vitreous with the exception of high iron and high lime slags.

Both very viscid and very fluid slags are undesirable, inasmuch as the former retain globules of matte and metal, whilst the latter do not come sufficiently in contact with the ore, especially if it is in somewhat coarse lumps. Silica is the great cause of viscosity, whilst iron and manganese increase the fluidity of a slag, but fluidity due wholly to iron is liable to cause an iron crust, and so occasion loss. Lime may or may not make a fluid slag, most high lime slags, however, flow smoothly. Fusibility is a very important property of a slag, and is increased by iron, manganese, lime, and by alumina if the silica is low, and rarely or never by manganese and zinc. It is diminished by silica and by alumina in presence of much silica. Refractory slags arise either from insufficient temperature or from injudicious combination of the charges. The closer certain recognised types are approached, the greater will be both the fusibility and fluidity of a slag. Increasing the number of elements in a slag generally makes it more fusible, hence mixing different ores is advantageous; this remark, however, does not apply to zinc, aluminium, and magnesium: the latter element for some unaccountable reason occasions great loss of silver.

All lead slags are magnetic, the author attributing this property to the presence of iron silicates and sulphides. The brittleness of these slags depends on the number, kind, and amount of the bases present; generally silica causes toughness, and bases brittleness, although the latter is not always true. Slags with less than 34 per cent. of silica are usually brittle, whilst those containing as much as 35 to 40 per cent. are tough, unless there is little iron and much lime (22 to 30 per cent.). Whenever there is much matte produced or when zinc is present in the ore, it is best not to have very brittle slags. Brittle slags are generally free from both silver and lead. Lead slags consist mainly of iron and calcium silicates, manganese, however, is frequently present, so are also zinc, aluminium, barium, and magnesium, but the last four are to be avoided as much as possible. Incidental constituents of lead slags are silver, lead, potassium, sodium, phosphorus, sulphur, sometimes copper, nickel, and cobalt; whilst Leadville slags frequently contain vanadium. In abnormal slags, quartz, ferric oxide, and quicklime are sometimes found. Delicate needles containing lead and sulphur are observed in the blistered cavities in the crust of pots of slags.

The author does not approve of decomposing the slags by fusion with sodium carbonate and nitrate in a platinum crucible, but if such a method is resorted to, the pulverised slag should be first treated with hydrochloric acid, evaporated to dryness, more hydrochloric acid added, filtered, and then fused with sodium carbonate; or, better, fuse the slag directly with potash in a silver crucible, or if silver is also to be determined, in a platinum crucible heavily plated with gold. The method generally followed by the author is to take the sample in the way already noted, pulverise and moisten about half a gram with water, add concentrated hydrochloric acid, and digest with a few drops of nitric acid, the silica can then be separated perfectly free from iron in the usual manner. Iron is determined by permanganate, calcium as oxalate or volumetrically, manganese by the bromine or zinc oxide methods, other constituents by the usual methods.

The success of smelting siliceous ores depends on the economic use of lime, iron, and manganese as fluxes, whilst the life or campaign of a furnace is greatly influenced by the judicious selection of slags; such inconveniences as the accumulation of silica, or iron, charcoal, coke, zinc, or lead crusts may be eliminated by the use of suitable slags for some time. Slags must of course be varied to suit the impurities in the ores to be dealt with, but from the author's experience and the careful and complete analyses of 100 slag samples, the results of which are given in a table, it is concluded that certain definite "slag types," or slags having some well-defined composition and a distinct crystalline form exist, and that the nearer slags in general approach to any of these types the more effectual they are. Taking the important constituents lime, iron and manganese, and silica, it is observed that the best slags range within the following limits per cent.: SiO_2 31 to 36, Fe + Mn 23 to 30, CaO 14 to 25: whilst the slags doing the best work and the longest campaigns do not vary beyond SiO_2 31 to 34, Fe + Mn 24 to 27, CaO 14 to 25. The limits SiO_2 26 to 41, Fe + Mn 18 to 35, CaO 5 to 35, would include all lead slags.

The seven types laid down by the author include practically every known slag which is well adapted for melting argentiferous lead, and are composed as follows as regards the most important constituents:—

Types.	A.	B.	C.	D.	E.	F.	G.
CaO	6	10	12	16	20	24	28
FeO + MnO...	52	45	50	34	40	33	27
SiO_2	32	35	28	34	30	33	35

Type A. Crystallises in rectangular plates; but is not adapted to lead melting as the iron is too high, the lime too low.

Type B. Forms generally small, rhombic plates more or less thickened and characterised by well-defined striations. This type of slag will keep the furnaces in good condition, it gives large yields, but is liable to cause large losses of lead and silver; it is not a bad slag in localities where limestone is dear.

Type C. Is black and distinctly crystalline, and has the formula $6\text{FeO}, 3\text{SiO}_2 + 2\text{CaO}, \text{SiO}_2$ assigned it. It is highly recom-

mended where iron flux is abundant, and the ores carry much zinc.

Type D. Can be represented by the formula $5\text{FeO}, 4\text{SiO}_2 + 3\text{CaO}, 2\text{SiO}_2$; it crystallises in more or less translucent, flattened prisms often with an abrupt arrow-shaped termination. It is well adapted to the treatment of siliceous and very impure ores.

Type E. Corresponds to the formula $6\text{FeO}, 3\text{SiO}_2 + 4\text{CaO}, 2\text{SiO}_2$; it crystallises in monoclinic prisms. This is an excellent slag and very economical where the fluxes are easily obtained.

Type F. This is a black, lustrous, distinctly resinous slag. The crystals are rectangular prisms, remarkably translucent and even transparent when there is a little manganese present; the crystals are frequently indented. It is very friable.

Type G. Crystallises in cubes. It is the best slag known for the treatment of very siliceous ores, and has been found successful with ores containing large quantities of baryta, alumina, and zinc. Generally slags intermediate or differing widely in composition from the above types, having botryoidal, pectolitic or wavelitic crystalline forms, or those which are devoid of crystalline structure, may be considered abnormal and untrustworthy for smelting purposes. Hexagonal crystals indicate too high a percentage of lime. Slender-needles result from fluxing highly siliceous ores with lime, and are accompanied by great loss of silver, but they contain no lead.

The proportion of lime seems to exert some influence on the crystalline structure of slags. The use of charcoal increases the tonnage, but generally with an increased loss of silver. These results show that certain ratios should exist between the silica and the bases of a slag, and that lime exerts a great cleansing influence on slags; but the problem why one slag is good and another of similar composition bad still remains to be answered. The author points out that loss of silver is due neither to the dissemination of globules of matte nor to the influence of manganese.

D. A. L.

Crystallised Halogen Salts of Mercury. By W. SIEVERS (*Ber.*, 21, 647—652).—Mercuric bromide is obtained in tetragonal plates when an excess of bromine is added with agitation to a slightly acid solution of mercuric nitrate of sp. gr. 1.197; hypobromous acid being formed in the reaction as noticed by Spiller (*Chem. News*, 6, 249). The chloride prepared in like manner forms slender needles. Mercuric iodide is obtained in red, tetragonal plates by adding to a boiling solution of mercuric nitrate rather more iodine than it can dissolve, and boiling for some time with constant replacement of the evaporated water.

A mixture of mercuric and mercurous chlorides is obtained by the action of chlorine on a solution of mercurous nitrate; this is washed with hot water to remove the mercuric salt, and the amorphous mercurous chloride crystallised from mercurous nitrate solution, when it forms yellowish-white, tetragonal plates. Crystallised mercurous

bromide and iodide have been already prepared by this method by Stroman (this vol., p. 111).
A. J. G.

Ferric and Aluminium Phosphates. By P. HAUTEFEUILLE and J. MARGOTTET (*Compt. rend.*, **106**, 135—138).—Glacial phosphoric acid at 100° dissolves 15 per cent. of ferric oxide or 8 per cent. of alumina, and if the solutions are kept at this temperature they deposit distinct crystals which are readily decomposed by water. They have the composition $\text{Fe}_2\text{O}_3, 3\text{P}_2\text{O}_5 + 6\text{H}_2\text{O}$ or $\text{Al}_2\text{O}_3, 3\text{P}_2\text{O}_5 + 6\text{H}_2\text{O}$. The ferric compound forms pinkish, rhombic plates, derived from a monoclinic prism; the aluminium compound forms colourless, prismatic crystals with longitudinal extinction.

If the solution is heated rapidly to 150—200°, and is kept at this temperature, the crystals contain only 4 mols. H_2O , and are not readily attacked by water or alcohol. The iron salt forms pinkish, nacreous, rectangular lamellæ, which act strongly on polarised light; the aluminium salt forms birefractive needles grouped in bundles.

Above 200°, the solution deposits crystals at a temperature which is lower the greater the proportion of basic oxide present. In all cases they have the composition $\text{Fe}_2\text{O}_3, 3\text{P}_2\text{O}_5$ or $\text{Al}_2\text{O}_3, 3\text{P}_2\text{O}_5$, but the form of the iron salt depends on the temperature at which crystallisation takes place. At 200—250°, it forms short, channelled, rhombic prisms; from 250° to incipient redness, fusiform, triclinic crystals; at a red heat, long, monoclinic prisms, sometimes with an almost square orthogonal section, and usually terminated by a rhombic face at an acute angle with the edge of the prism.

At 200°, the aluminium phosphate separates in tetrahedra with curved faces, without sensible action on polarised light; at 250°, the crystals are octahedra, frequently modified by faces of the cube. This form is stable up to a red heat. If the phosphate crystallises at a red heat, or is obtained by the action of phosphoric acid on corundum, it separates in cubes which are not modified, but are frequently macle. From these results, it seems that the anhydrous aluminium phosphate always crystallises in the regular system, but the exact form depends on the temperature. These differences are comparable with the differences observed in the case of ferric and silicon phosphates.
C. H. B.

Volume and Carbon Contents of the Gas Evolved during Solution of Iron in Acids. By H. BÄCKSTRÖM and G. PAJKULL (*Zeit. anal. Chem.*, **26**, 683—689).—That different kinds of iron evolve different volumes of gas when dissolved in acid was ascertained by Bergman in 1781, and these differences were connected by Vandermonde, Berthollet, and Monge, with the differences in the amount of carbon present.

The authors have determined the total volume of gas, and the quantity of carbon in it, from 14 samples of iron containing carbon (total) ranging from 0.11 to 4.24 per cent. As a general rule, the more highly carburetted the iron, the smaller is the volume and the greater the carbon-contents of the gas evolved, but the relation is not a quantitative one in either case. No definite fraction of the

combined carbon is evolved as a gaseous hydrocarbon. Part of the carbon invariably remains dissolved in the acid as an organic substance capable of reducing permanganate, so that the results of titration are too high as well as variable. Bergman asserted that sulphuric and hydrochloric acids evolved equal volumes of gas, but in a special experiment on a white cast iron containing 3.87 per cent. of carbon, a volume of gas larger, and containing more carbon, was obtained with hydrochloric acid than with sulphuric acid of corresponding strength.

It is well known that hardened steel leaves less residue than unhardened when dissolved in acids. Cold hammered steel behaves like hardened steel. The latest view of the constitution of steel is that it contains a true carbide of iron forming a mass of cellular texture, the pores of which are filled with pure iron. According to Osmond and Werth, the so-called cement-carbon (*Cement-Kohlenstoff*, *carbone de recuit*) is that which exists in the carbide in combination with iron, whilst the hardening-carbon (*Härtungs-Kohlenstoff*, *carbone de trempe*) exists in solution in the iron disseminated in the cellular nuclei. The latter may therefore be expected to be converted more or less into gaseous hydrocarbons, whilst the former would more or less remain undissolved on treatment with acid. It is found that hardened steel gives both a larger volume of gas, and one richer in carbon than the same steel before hardening. It seems as though almost the whole of the hardening carbon is evolved as gas. The effect of cold hammering is, however, both as to volume of gas and amount of carbon, exactly the reverse. M. J. S.

Action of Sea-water on Cast Iron. By C. N. DRAPER (*Chem. News*, 56, 251).—A specimen of cast iron, weighing 557.31 grams, and measuring 85 mm. × 52 mm. × 20 mm., was broken from a rail which had been exposed to the alternate action of sea-water and the atmosphere for about 50 years. The lateral surfaces were slightly coated with oxide, and the upper surface consisted, to a depth of 7 mm., of a brownish-grey, graphitoid substance, amounting to 67.59 grams, and containing 23.6 per cent. of carbon along with much unoxidised iron, presumably existing as FeC_3 . The graphitoid substance was easily removed from the specimen with a knife, leaving a clean, bright, metallic surface exposed. This operation was accompanied by a distinct rise in temperature. D. A. L.

Influence of Phosphorus on Iron. By L. SCHNEIDER (*Dingl. polyt. J.*, 266, 378—382).—According to Cheever, the variable effect of phosphorus on iron is explained by assuming that the phosphorus is present in the metal in two forms, as "phosphate" and "phosphide," which influence the properties of iron in different ways. This assumption is based on the analytical results obtained in a series of experiments in which the iron was treated with a cold ammoniacal solution of cupric chloride, the residue being digested with an alkaline solution of ammonium oxalate, or shaken for five minutes with a 1 per cent. solution of hydrochloric acid, and the phosphoric acid determined in the solution. Cheever assumes that the small amount of phosphide

existing in the metal completely resists the action of cupric chloride, and that the complete solution of all phosphates formed from phosphides at a red heat is effected either by a treatment with a 1 per cent. solution of hydrochloric acid for five minutes, or by the action of an ammoniacal solution of ammonium oxalate.

The author criticises Cheever's method of examination, and the conclusions deduced therefrom. He shows that iron phosphide in iron is affected by cupric chloride in the cold, and if the solution is quite neutral the phosphoric acid obtained by the oxidation of the phosphide remains in the residue, from which it may be subsequently extracted with ease by weak acids.

D. B.

Vapour-density of Ferric Chloride at Various Temperatures.

By W. GRÜNEWALD and V. MEYER (*Ber.*, **21**, 687—701).—In these experiments, sublimed ferric chloride was used. The estimations were made in a slightly modified form of V. Meyer's apparatus, in which the bulb, 45 mm. in diameter, was reduced to a length of only 125 mm., whilst the whole apparatus was 670 mm. high; by this means, the whole of the bulb acquired the temperature of the bath. For greater convenience in filling with nitrogen, a thin tube was fused into the bottom of the bulb, bent so as to follow the shape of the bulb and stem until the side tubes were nearly reached, then bent at right angles to connect with the nitrogen supply.

A new device of Meyer and Biltz for the introduction of the substance is also described:—On the stem, opposite to, but just below the delivery tube, a short side tube is fused; through this passes a glass rod whose end projects across the stem; the joint between rod and side tube being made with well-fitting caoutchouc tubing. The little bottle containing the substance rests on the end of the rod; when the bulb has attained the required temperature, the rod is slightly withdrawn, and the bottle falls into the bulb.

Four determinations at 448° (in sulphur vapour) gave a density of 10·487, whilst that required by the formula Fe_2Cl_6 is 11·2. After the estimation, the contents of the bulb did not give the slightest reaction for ferrous salt. Experiments at a lower temperature were out of the question, as even in these the vaporisation was rather slow.

At 518° (in vapour of phosphorus pentasulphide), three experiments gave a vapour-density of 9·569; about $\frac{1}{10}$ of the iron was found to be in the ferrous condition after the estimation.

At 606° (in vapour of zinc chloride), in a smaller apparatus, six experiments gave a mean vapour-density of 8·383; about $\frac{1}{8}$ of the iron was in the ferrous state at the close.

The determinations at higher temperatures were effected in platinum apparatus heated in a Perrot's gas furnace. The mean of three estimations at about 750° gave a vapour-density of 5·406, whilst about $\frac{1}{3}$ of the iron was found to be in the ferrous state at the close of the experiments. At about 1050°, the numbers obtained for the density were 5·3 and 4·9; $\frac{1}{3}$ and $\frac{1}{2}$ of the iron being respectively found in the ferrous state. The results at 1300° were practically identical with those at 1050°. As it seemed probable that the lower results in the higher temperature experiments might be due to the action of the

platinum on the ferric chloride, experiments were made in platinum apparatus at about 600° , but the results obtained were in agreement with those previously got in glass.

With regard to the amounts of ferrous salt observed at the end of the experiments, it must be remembered that this does not show the amount of dissociation that occurred at the temperature of the experiment, inasmuch as recombination occurs on cooling.

Experiments in a chlorine atmosphere at the temperature of boiling sulphur and boiling phosphorus pentasulphide respectively, gave practically the same results as those in an atmosphere of nitrogen.

From these results, it follows that ferric chloride does not at any temperature show a vapour-density sufficiently high for the molecular formula Fe_2Cl_6 , whilst at 750° and 1077° numbers were obtained not far removed from 5.6, the calculated vapour-density for the molecular formula FeCl_3 .
A. J. G.

Use of Hydrogen Sulphide to Purify Nickel and Cobalt. By H. BAUBIGNY (*Compt. rend.*, **106**, 132—135).—The only possible method of separating nickel and cobalt by means of hydrogen sulphide is to saturate the solution of the sulphates with the gas at 0° , and heat to 100° . Nickel sulphide is precipitated, but cobalt sulphate is not decomposed. The precipitate, however, always contains a notable proportion of cobalt even when the quantity of free acid is almost sufficient to prevent the precipitation of the nickel. Dellf's method of precipitating cobalt as sulphide from the acetate by mixing a solution of the nitrates or sulphates with a quantity of sodium acetate not quite sufficient to convert all the cobalt into acetate, is not satisfactory, since a considerable proportion of the nickel is precipitated at the same time.
C. H. B.

Alloy of Titanium, Silicon, and Aluminium. By L. LÉVY (*Compt. rend.*, **106**, 66—68).—10 grams of titanium, 35 grams of aluminium, 35 grams each of fused sodium and potassium chlorides, were heated in a Perrot's furnace in a porcelain crucible enclosed in a crucible brasqued with charcoal and rutile, a current of dry hydrogen being passed into the inner crucible. The product was treated with water and then with dilute acid, and a residue was obtained consisting of lustrous, steel-grey lamellæ, with angles of 90° , very brittle, and good conductors of heat, sp. gr. at $16^{\circ} = 3.11$. They do not alter in air or nitrogen oxides at the ordinary temperature, but tarnish when heated, and burn if heated in oxygen. They are not attacked by vapours of sulphur, selenium, phosphorus, or arsenic, but burn in chlorine or in vapour of iodine or bromine, especially the former. Liquid bromine, however, is without action. Superheated steam and cold fuming nitric acid have no action, but hot nitric acid attacks the crystals slightly. Hydrochloric and sulphuric acids act somewhat in the cold and more readily when heated. The crystals burn when heated in hydrogen chloride, and dissolve readily in aqua regia, but are not dissolved by hydrobromic and hydriodic acids, or by mixtures of these acids with nitric acid. Sulphuric acid and calcium fluoride have little action, and potash only partially dissolves

the crystals in the cold, but dissolution is complete on heating, with evolution of hydrogen. The crystals have the composition $\text{Al } 71.06$; $\text{Ti } 26.65$; $\text{Si } 2.19$; loss (? C) 0.10 , which agrees with the formula $(\text{Ti} : \text{Si})\text{Al}_4$, and hence it is probable that they are mixtures of the isomorphous compounds, TiAl_4 and SiAl_4 .

If zinc or magnesium is substituted for aluminium, no crystals are obtained.
C. H. B.

Titanium Trioxide. By A. CLASSEN (*Ber.*, **21**, 370—372).—The action of hydrogen peroxide on titanium dioxide (compare Piccini, *Abstr.*, 1882, 808; 1883, 1054; Weller, *Abstr.*, 1883, 295) has been studied by the author, who recommends the following method for obtaining the product:—Pure titanium chloride is added drop by drop to dilute alcohol, and the clear and very dilute solution is treated with a large excess of hydrogen peroxide. Ammonia, ammonium carbonate, or aqueous potash is added to the solution with the production of a yellow or, in the case of ammonia, of a reddish-yellow liquid, which after some time yields a yellow precipitate. This is allowed to subside, the clear solution siphoned off, and the precipitate repeatedly washed by decantation; the compound, however, tends to retain water and salts in considerable quantities. When dried on a tile, it approximates to the composition $\text{TiO}_3 + 3\text{H}_2\text{O}$.

W. P. W.

Antimony Pentachloride. By R. ANSCHÜTZ and P. N. EVANS (*Proc. Roy. Soc.*, **42**, 379—387; compare *Trans.*, 1886, 379).—The authors find that, contrary to the statement of Daubrawa (this *Journal*, 1877, ii, 406), SbOCl_3 is not formed when water is added to antimony pentachloride, nor is any hydrogen chloride evolved. The antimony pentachloride is best dissolved in chloroform, and the calculated amount of water added. Under these circumstances a crystalline substance, $\text{SbCl}_5 \cdot \text{H}_2\text{O}$, soluble in chloroform, is obtained, melting at 87 — 92° . It is very hygroscopic, and diliquesces to a clear liquid, which crystallises over sulphuric acid in broad crystals, described by Daubrawa as the oxychloride. When distilled, it gives SbCl_5 , SbCl_3 , and a waxy residue.

A chloroform solution of antimony pentachloride, when heated with water in a sealed tube, gives antimony trichloride and phosgene gas. Phosgene gas is also produced by heating a chloroform solution of the monohydrate at 100° .

Antimony pentachloride tetrahydrate can be produced in the same way as the monohydrate. It is a crystalline mass, insoluble in chloroform. By adding anhydrous oxalic acid to a chloroform solution of antimony pentachloride, the authors obtain a substance, $\text{Sb}_2\text{Cl}_6\text{C}_2\text{O}_4$, probably $\text{C}_2\text{O}_2(\text{O} \cdot \text{SbCl}_4)_2$. It crystallises from chloroform in tables melting at 148.5 — 149° , and is decomposed by water with liberation of oxalic acid.

The difference in behaviour with carbon compounds between phosphorus pentachloride and antimony pentachloride is attributed to the property of the latter of combining with water instead of decomposing it.
H. K. T.

Redetermination of the Atomic Weight of Platinum. By W. DITTMAR and J. MCARTHUR (*J. Soc. Chem. Ind.*, **6**, 799—803).—The value $Pt = 194.8$ which Seubert (*Abstr.*, 1881, 514) deduced from his analyses of platinochlorides, is too low; his own analyses, if properly interpreted, show that the true value lies, by a considerable fraction of a unit, higher. According to the authors' analysis of potassium platinochloride, the true "Pt," although probably a shade below, lies close to 195.5. Taking "Pt" as meaning the number which must be substituted for Pt in the calculation of the ratios $2KCl : PtCl_6K_2$; $2KCl : Pt$, &c., in order to obtain the correct factors for reducing analytically obtained platinochloride to potassium chloride, &c., even the number 195.5 is too low, 196 affording in general a better approximation. But Pt if taken in this sense is no constant at all. Those factors must be determined directly by standard experiments. The results of the authors' own standard experiments are given and contrasted with the theoretically calculated ratios in the subjoined table. The entries "Ta" refer to Tatlock's methods; those "F" to the authors' form of Finkener's method described in detail in the original paper, and those marked "N" to the usual platinum process for the determination of ammonia:—

Method.	Theoretical factors.				Dittmar and McArthur's empirical factors.	Notes.
	Symbols.	Values calculated for				
		Pt = 194.8	195.5	196		
Ta	2KCl : PtCl ₆ K ₂	0.30707	0.30665	0.30633	0.30627	(1)
Ta	2KCl : Pt	0.76571	0.76307	0.76112	0.76016	(2)
F	2KCl : Pt	0.76571	0.76307	0.76112	0.76084	(1)
N	2NH ₄ Cl : PtCl ₆ (NH ₄) ₂ ..	0.24123	0.24084	0.24057	0.23890	(3)
N	2NH ₄ Cl : Pt	0.54934	0.54737	0.54598	0.54590	(4)

Notes. (1) Refers to the potassium chloride in the substance, (2) to that in the platinochloride precipitate, and (3) and (4) to the ammonium chloride to be determined, not to that contained in the platinochloride precipitate.

D. B.

Hydroxylamine Platinum Bases. By H. ALEXANDER (*Chem. Centr.*, 1887, 1254—1255).—As the platinum bases mentioned below are all explosive, the platinum and chlorine cannot be determined by heating the compound. The platinum was determined by moistening a quantity of the substance with concentrated sulphuric acid in a platinum capsule, evaporating off the acid and finally dispelling any remaining acid by the addition of ammonium carbonate. The chlorine was determined by distilling the compound with sulphuric acid, and passing the resulting hydrogen chloride into a solution of silver nitrate.

Platoso-dihydroxylamine hydrochloride, $\text{Pt}(\text{NH}_3\text{O}\cdot\text{NH}_3\text{OCl})_2$, which Lössen has already described, is obtained by the action of potassio-platinous chloride on hydroxylamine hydrochloride. Strong bases precipitate *platoso-dihydroxylamine hydroxide*, $\text{Pt}(\text{OH})_2\cdot 4\text{NH}_3\text{O}$, from solutions of the chloride. The oxalate, $\text{PtC}_2\text{O}_4\cdot 4\text{NH}_3\text{O}$, is prepared from neutral potassium oxalate and the chloride; an acid salt does not seem to exist. *Platino-dihydroxylamine sulphate*, $\text{PtSO}_4\cdot 4\text{NH}_3\text{O} + \text{H}_2\text{O}$, can be prepared from this oxalate by the action of weak sulphuric acid; the sulphate is more easily prepared from the free base and sulphuric acid. A phosphate was obtained, but no nitrate.

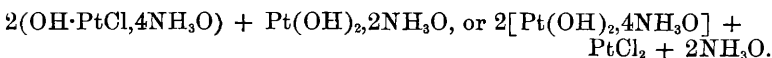
Platoso-dihydroxylamine hydrochloride platinous chloride is prepared by the addition of platinous hydrochloride to the chloride.

Platoso-hydroxylamine hydrochloride, $\text{Pt}(\text{NH}_3\text{OCl})_2$, is formed by the action of hydrochloric acid, on either platino-dihydroxylamine hydrate when warm, or on the corresponding chloride.

The compound formed by the action of ammonia on platinous hydrochloride and on *platoso-hydroxylamine hydrochloride*, which has been described by Jörgensen, the author regards as *platoso-hydroxylamine ammonium chloride*, $\text{Pt}(\text{NH}_3\text{O}\cdot\text{NH}_3\text{Cl})_2$.

The double salt, $\text{Pt}(\text{NH}_3\text{O}\cdot\text{NH}_3\text{Cl})_2\cdot\text{PtCl}_2$, is obtained from platinous hydrochloride and *platoso-hydroxylamine ammonium chloride*, as well as from the above-named mixed chlorides and potassio-platinous chloride.

Free hydroxylamine acting on platinous chloride gives rise to the compound $\text{OH}\cdot\text{PtCl}_2\cdot 4\text{NH}_3\text{O} + 2\text{H}_2\text{O}$, which explodes at 140—150°. Another compound which may be regarded as platinum nitrogen chloride, PtNCl , together with the double salt,



were also obtained.

Free hydroxylamine acting on platinous hydrochloride gives rise to a compound corresponding approximately with the formula $\text{PtCl}_2\cdot 4\text{NH}_3\text{O}$, and by its action on potassio-platinous chloride to a base $\text{Pt}(\text{OH})_2\cdot 2\text{NH}_3\text{O}$, which has not been obtained quite pure as yet.

J. P. L.

Ruthenium Oxides. By H. DEBRAY and A. JOLY (*Compt. rend.*, 106, 100—106).—The authors prepared crystallised ruthenium dioxide by heating the amorphous oxide in a vacuum or by heating the metal in oxygen. It forms quadratic prisms with the faces m , h' , a' , and b' . The ratios being $b : h :: 1000 : 692\cdot 43$, and hence is isomorphous with cassiterite and rutile. The faces in the zone $m h'$ are often striated as in those minerals, and very frequently the crystals are maced after the cassiterite and rutile types.

When heated to bright redness in a muffle, ruthenium absorbs oxygen, but after some time absorption takes place very slowly, and the metal is never fully oxidised to the dioxide. If, however, the product is powdered and again heated, the dioxide is obtained crystalline, with an indigo-blue colour. The authors were unable to obtain the sesquioxide in the manner described by Claus.

When ruthenium is heated in oxygen at a temperature above the

melting point of silver, it is entirely converted into crystalline products, and a portion volatilises and condenses in crystals. If the current of gas is rapid, the odour of ozone or ruthenium peroxide is perceived, and a certain quantity of the peroxide can be condensed in a flask cooled by ice. The inside of the tube is lined with ruthenium dioxide and a small quantity of a black substance which seems to contain more oxygen than the dioxide. The products are similar to those obtained when ruthenium peroxide and nitrogen are passed through a red-hot porcelain tube, and they are distributed in the same manner. The dioxide is found in the cooler parts of the tube, which indicates that the peroxide formed at about 1000° decomposes at a lower temperature. At temperatures above 1000° , ruthenium dioxide has a considerable tension of dissociation, and in a vacuum is partially reduced to the metal, a small quantity of the peroxide being formed. At a bright red heat, the phenomena are similar.

The authors were unable to obtain an oxide lower than the dioxide.

Ruthenium peroxide is formed at about 1000° , and decomposes with explosion when cooled to 108° , but can be isolated by rapid cooling. It affords another instance of a compound which is decomposed by heat, and yet is formed at a high temperature. The crystallisation of the dioxide is a phenomenon of apparent volatilisation, and the formation of the peroxide is analogous to the formation of ozone, silicon hexachloride, silver oxide, hydrogen selenide or telluride, &c.

The formation of ruthenium peroxide, like the decomposition of water, is endothermic.

C. H. B.

Mineralogical Chemistry.

A New Zealand Sulphur Island. By R. W. E. MACIVOR (*Chem. News*, **56**, 251—253).—White Island, in the Bay of Plenty, New Zealand, is part of the crater of a huge, submerged, conical volcano. Part of the island disappeared during the volcanic disturbances in New Zealand a year or two ago. The mineralogical and other characters of the place in 1883 were such as are general in volcanic regions; special features were heaps of gypsum with from 30 to 85 per cent. of sulphur, and curious hollow spheres, some as large as old-fashioned bombshells, consisting of an exterior crust of gypsum and a little sulphur, with transparent crystals of prismatic sulphur inside. There were active geysers and fumeroles sending out hydrogen chloride and steam, and ejecting with great violence transparent lumps of sulphur varying in colour from orange to a reddish-brown, although the sulphur deposited around the orifices was pale yellow and opaque; the depth of colour is due to selenium; some specimens contain as much as 1·75 to 2·1 per cent., which render it unfit for the manufacture of sulphuric acid. In the neighbourhood of the fumeroles there were many large holes full of thin, black, boiling mud consisting of clay, siliceous matter, gypsum, and iron pyrites suspended in strongly acid

water containing more mineral matter than the water from the lake. Lake Hope, in the midst of the central amphitheatre, had a fairly uniform depth, but was unfathomable near the centre; its temperature was 68° ; it was muddy in the centre, but transparent, and of blue-green colour elsewhere; the atmosphere over it was very irritating owing to the constant evolution of hydrogen chloride; the bottom of the lake wherever visible was covered with oblique crystals of selenite. Analysis of the water yielded the following results per 1000 parts:—

FeSO ₄ .	Al ₂ (SO ₄) ₃ .	CaSO ₄ .	MgSO ₄ .	K ₂ SO ₄ .	Na ₂ SO ₄ .	Al ₂ Cl ₆ .
15·254	1·350	3·605	0·931	4·715	10·033	25·557
	NaCl.	SiO ₂ .	HCl.	Water, &c.		
	11·950	0·67	149·876	776·059		

It is suggested that the sulphur and hydrogen chloride result from the action of sea-water on hot beds of pyrites inside the mountain.

D. A. L.

Graphite from the Bagoutal Mountains, Siberia. By W. H. COLLINS (*Chem. News*, 57, 36).—Four samples of graphite from this region were analysed and gave the following mean results per cent.:—C, 38·91; SiO₂, 38·83; Al₂O₃, 13·86; CaO and MgO, 2·12; Fe₂O₃, 4·52; loss and volatile matter, 1·77. This graphite is employed for crucible making with excellent results. It is somewhat similar in character to the graphite from the Stephanovsky mine.

D. A. L.

Gold Quartz from the Transvaal. By P. HOLLAND (*Chem. News*, 56, 271—272).—The specimen weighed 18 grams; it was a greenish-grey, dark-coloured, massive quartz with iron-stained fissure. In sections, under the microscope, F. Rutley detected “allotriomorphic” quartz crystals, cubes of pyrites, gold, numerous liquid lacunæ, particles of mica, and patches, probably, of felspar. On heating in an open tube, sulphurous anhydride was given off. For analysis the mineral was decomposed with hydrofluoric acid, and gave the following numbers:—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeS ₂ .	Au.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	C.
92·86	2·86	1·22	0·27	0·03	0·18	1·40	0·41	0·58	a little.

D. A. L.

Braunite from Jakobsberg. By M. SCHUSTER (*Zeit. Kryst. Min.*, 13, 621—623, from *Tschermak's Min. Mitth.*, 7, 443—451).—This mineral, discovered by Igelström (Abstr., 1887, 643) at the Jakobsberg manganese mines, Wermland, Sweden, has been subjected by the author to a careful crystallographical examination. Braunite, he finds, is not tetragonal, as stated by Igelström, but rhombohedral, tetartohedral, and isomorphous with iron glance and titaniferous iron ore.

B. H. B.

Chrome Iron Ore in Australasia. By R. W. E. MACIVOR (*Chem. News*, 57, 1—2).—Chrome iron ore is found in New Zealand in two or three places, but chiefly near Nelson, in the middle island,

where it is associated with serpentine and olivine rocks ; it is obtained in three forms : (1.) *Massive crystalline* in highly crystalline black bands, showing on fracture distinct planes of octahedron, and containing from 52 to 65 per cent. of chromic oxide. (2.) *Massive amorphous*, brownish-black bands, longer, broader, and softer than the preceding, in which Cr_2O_3 = from 30 to 51 per cent. (3.) *Disseminated crystalline*, in which nodules of moderately constant composition, 56 to 69 per cent. Cr_2O_3 , are more or less evenly distributed through the serpentine, forming in some cases as much as 90 per cent., in others only 20 per cent. of the rock, giving it the appearance of a conglomerate. On exposure to the air, the binding material disintegrates and the nodules are easily separated ; in some cases, the preliminary weathering may be dispensed with.

Chrome iron ore is also found in New Caledonia, in New South Wales, in Queensland, and in Tasmania. D. A. L.

Genesis of the Plumbiferous Phosphates and Arseniophosphates of Roure and de Rosiers, Pontgibaud. By F. GONNARD (*Compt. rend.*, 106, 75—77).—These minerals occur in the neighbourhood of apatite and lead carbonate. It is known that water containing carbonic anhydride will dissolve both lead carbonate and apatite, and it is probable, therefore, that the lead phosphate or arseniophosphate has been formed by the interaction of these substances or by the action of the water containing apatite on galena.

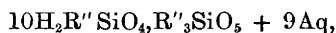
C. H. B.

Mineralogical Observations in Styria. By E. HATLE and H. TAUFES (*Chem. Centr.*, 1887, 1264—1365, from *Verh. geol. Reichsanst.*, 1887, 226—228).—(1.) *Pharmacolite from Völleg*.—This mineral, which is new to Styria, has been found in large (5 mm.) crystals and in spheroidal groups and crusts on iron pyrites, magnetic pyrites, and arsenical pyrites, blende, galena quartz, and calcspar ; it contains—

As_2O_5 .	CaO.	H_2O at 110° .	H_2O at red heat.	Total.
48·60	27·04	12·34	12·15	100·13

Albite in twin crystals has likewise been found in the neighbouring lead mine of Kaltenegg.

(2.) *Iron Deweylite from Kraubach*.—This scarlet-red mineral, obtained from serpentine in Leising, corresponds with the formula $10\text{H}_2\text{MgSiO}_4 \cdot \text{Mg}_2\text{FeSiO}_5 + 9\text{H}_2\text{O}$. As many other deweylites contain the same amount of water, the authors suggest the following general formula for deweylites :—



in which $\text{R}'' = \text{Mg}$, which is in part displaceable by Fe, Ni, &c.

J. P. L.

New Discoveries of Minerals. By H. v. FOULLON (*Zeit. Kryst. Min.*, 13, 631—632, from *Verhdl. k. k. geol. Reichsanst.*, 1886, 464).—At Klausen, in Tyrol, a greenish-blue mineral has been found as a thin coating on mica-schist and quartzite, in association with gypsum,

felsöbanyite, malachite, and allophane. This greenish-blue coating, undoubtedly of recent formation, is a mineral mixture, of which 54 per cent. consists of a hydrated copper sulphate, langite, $\text{CuSO}_4 \cdot 4\text{H}_2\text{O}$, in all probability a product of the alteration of copper pyrites.

At the same locality, calcite of recent formation has been found. It occurs in an old adit-level, in the form of white or yellow imperfect crystals, and attains a thickness of 4 cm. In the Reussen lode, at Kuttenberg, in Bohemia, the rare mineral cronstedtite has recently been found in well-developed crystals. B. H. B.

Ilmenite from the Ardennes. By C. KLEMENT (*Zeit. Kryst. Min.*, **13**, 626—627, from *Tschermak's min. Mitth.*, **8**, 1).—Ilmenite from the phyllite of Rocroi gave on analysis the following results:—

SiO_2 .	TiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MnO .	CaO .	K_2O .	Na_2O .	Total.
2.14	52.21	1.83	3.52	27.16	13.60	0.43	0.23	0.19	101.31

Neglecting the admixed rutile and silicates, the formula of the ilmenite is RTiO_3 , in which $\text{R} = \text{Fe, Mn}$ in the proportion of 2 : 1. B. H. B.

Synthesis of Pyrrhotine. By C. DOELTER (*Zeit. Kryst. Min.*, **13**, 624—626, from *Tschermak's min. Mitth.*, **7**, 535—545).—The author has endeavoured to prepare magnetic pyrites (pyrrhotine) synthetically, and by means of analyses of the artificial mineral and of the pyrrhotine recently found at Schneeberg, in Tyrol, to elucidate the constitution of this mineral. The first experiment, in which ferrous chloride was heated with water containing sodium carbonate, and saturated with hydrogen sulphide, in a closed tube at 80° for three months, was unsuccessful, inasmuch as the pyrrhotine formed was decomposed on washing, a powder resembling limonite being produced. In the second experiment, ferrous chloride was treated under the same conditions in a closed rifle-barrel at 200° for 16 days. In consequence of the air remaining in the barrel, iron pyrites was formed as well as pyrrhotine; but when the filling of the barrel was effected in an atmosphere of hydrogen sulphide and carbonic anhydride, pyrrhotine was formed in small, hexagonal, brown, magnetic tablets, which on analysis gave results corresponding with the formula $\text{Fe}_{11}\text{S}_{12}$. A product similar in appearance was obtained on treating a mixture of ferrous chloride and zinc chloride in the same way at 200° for three weeks, the powder obtained giving on analysis results corresponding with the formula $\text{R}_{11}\text{S}_{12} = \text{Fe}_{11}\text{ZnS}_{11} = 2(\text{Fe}_{11}\text{S}_{12}) + \text{ZnS}$. Possibly this is a mechanical mixture of pyrrhotine and wurtzite. From these experiments, the author concludes that pyrrhotine is formed in nature at a low temperature, about 100° , from ferrous salts dissolved in water by the action of hydrogen sulphide in the presence of carbonic acid or reducing hydrocarbons. Further experiments were made in the dry way, ferrous chloride being heated in a stream of hydrogen sulphide in a glass tube from which the air had previously been expelled by a current of carbonic anhydride. Crystals having the formula $\text{Fe}_{11}\text{S}_{12}$ were obtained.

In conclusion, the author gives the following analysis of pyrrhotine recently found at the Schneeberg, in Tyrol:—

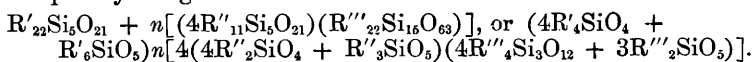
Fe.	S.	Co.	Total.
61·77	39·10	trace	100·87

These results correspond with the formula $\text{Fe}_{11}\text{S}_{12}$, or $10\text{FeS} + \text{FeS}_2$, a formula which was deduced from the analyses of all the artificial pyrrhotines prepared by the author. B. H. B.

Composition of Idocrase. By C. RAMMELSBURG (*Zeit. Kryst. Min.*, 13, 640—642, from *Zeit. deutsch. geol. Ges.*, 38, 507).—The recent analyses of idocrase (vesuvian), by v. Lasaulx, Ludwig, and Jannasch, have induced the author to analyse again the idocrase of Ala and Wilui, and to determine the formulæ with greater accuracy. The old theory of the general constitution of idocrase, $4\text{R}'_4\text{SiO}_4 + \text{R}'_6\text{SiO}_5 = \text{R}'_{22}\text{Si}_5\text{O}_{21}$, still holds good. It has, however, been simplified to a certain extent, since in idocrase $\text{R}'' : \text{R}'''_2 = 4 : 1$. The ratio of $\text{R}' : \text{R}''$, however, is variable, so that all varieties of idocrase may be divided into four classes, in which—

- (1.) $\text{R}' : \text{R}'' = 1·66 : 4 = 1 : 2·4$
- (2.) $\text{R}' : \text{R}'' = 1·33 : 4 = 1 : 3$
- (3.) $\text{R}' : \text{R}'' = 1·00 : 4$
- (4.) $\text{R}' : \text{R}'' = 0·5 : 4 = 1 : 8$.

Consequently the general formula is



To Class 1 belong the idocrase of Ala and Gleinitz, near Jordansmühl, in Silesia; to Class 2, those of Monzoni, Zermatt, Johnsberg in Silesia, Kedabek in the Caucasus; to Class 3, those of Vesuvius, Haslau near Eger; to Class 4, those of Wilui (in which the presence of boron was detected by Jannasch).

Idocrase and epidote are very similar in composition—

Epidote	$2\text{R}'_4\text{SiO}_4 + \text{R}'_6\text{SiO}_5$
Idocrase	$2\text{R}'_4\text{SiO}_4 + \text{R}'_6\text{SiO}_5$.

B. H. B.

Canadian Minerals. By B. J. HARRINGTON (*Zeit. Kryst. Min.*, 13, 651, from *Trans. R. Soc. Canada*, 1886, 81).—The author gives the results of analyses of sodalite (I) from the nepheline-syenite of Montreal, and (II) from the Ice River, Rocky Mts.:—

	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO .	Na_2O .	K_2O .	Na .	Cl .	Total.	Sp. gr.
I.	37·52	31·38	trace	0·35	19·12	0·78	4·48	6·91	100·54	2·22
II.	37·50	31·82	0·01	—	19·34	0·27	4·61	7·12	100·67	2·29

The mineral, termed *huronite* by Thomson, from the diabase of Drummond Island, in Lake Huron, is found by the author to be an impure or altered felspar, probably anorthite. B. H. B.

Felspar and Olivine from Syria. By B. DOSS (*Zeit. Kryst. Min.*, **13**, 624, from *Tschermak's min. Mitth.*, **7**, 461—534).—The author analysed two specimens of felspar from plagioclase-basalts; I, from Schuhba; II, from Chirbet Hôjet Sâlâ:—

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	CaO.	MgO.	$\overbrace{\text{K}_2\text{O. Na}_2\text{O.}}$	Total.
I.	51·26	31·49	0·33	trace	13·13	0·45	3·60	100·26
II.	50·23	31·88	0·20	trace	14·60	0·26	3·44	100·61

Plagioclase I is a labradorite, with the ratio Ab : An = 1 : 2 (8:17); plagioclase II is a labradorite, with the ratio Ab : An = 2 : 5. The olivine in these plagioclase-basalt-lavas usually occurs in twin-crystals, ∞P being in some cases the twinning-plane. B. H. B.

Albite of the Kásbek. By M. SCHUSTER (*Zeit. Kryst. Min.*, **13**, 614—615, from *Tschermak's min. Mitth.*, **7**, 373—399).—The determinations of the direction of extinction on P in the theoretically pure albite of the Kásbek in the Caucasus, recorded by Bärwald (*Zeit. Kryst. Min.*, **8**, 48), differ so entirely from those given by the author in his well-known work on the optical properties of the plagioclases, as to induce him to make a new investigation of this albite, using material chemically identical with that employed by Bärwald. His measurements of the angles of the crystals show that the discrepancy is caused by Bärwald having confused the right and left prisms.

B. H. B.

Anorthite from Saint-Clément. By A. LACROIX (*Zeit. Kryst. Min.*, **13**, 646, from *Bull. soc. fran. min.*, **9**, 46).—In the anorthite-gabbro of Saint-Clément, department Puy-de-Dôme, the author found the following minerals: titanite, idocrase, bright-green pyroxene, partly converted into actinolite, and anorthite twinned according to the albite and pericline law. The anorthite gave on analysis:—

SiO ₂ .	Al ₂ O ₃ .	CaO.	Na ₂ O.	Total.
46·05	35·10	18·32	(0·53)	100·00

As secondary minerals, there occur wollastonite, epidote, quartz, talc, and calcite. B. H. B.

Beryl from the Ifinger. By M. SCHUSTER and R. PRZIBRAM (*Zeit. Kryst. Min.*, **13**, 623—624, from *Tschermak's min. Mitth.*, **7**, 455—458; **8**, 190).—In 1883, beryl was discovered in mica-schist, on the north side of the Ifinger, near Meran. The crystals are sometimes as much as 18 cm. long and 34 cm. in circumference. Analysis gave the following results:—

SiO ₂ .	Al ₂ O ₃ .	BeO.	CaO.	MgO.	H ₂ O.	Total.	Sp. gr.
66·49	23·01	9·30	0·54	0·54	0·04	99·92	2·69

B. H. B.

Micas of the Pegmatite-Granite of Schüttenhofen. By R. SCHARIZER (*Zeit. Kryst. Min.*, **13**, 449—473).—At Schüttenhofen, a deposit of pegmatite-granite occurs intercalated in magnesian lime-

stone. The minerals, 18 in number, forming this rock separate into three typical associations or zones. Only one mineral, grey quartz, occurs in all three zones. The first zone, which forms the principal portion of the pegmatite deposit, consists of microcline, lepidomelane, and silver-white to tombac-brown muscovite, with the phosphates apatite, monazite, and xenotime. The second zone is formed of white albite, yellowish-white muscovite, bluish-black tourmaline, and brown manganese-garnet, with small quantities of light-green tourmaline. In the third zone appear typical lithium minerals: blood-red lepidolite, dark-green and pink tourmaline, with bluish-white albite (clevelandite). The variously coloured micas gave on analysis the results given in the accompanying table:—

	I.	II.	III.	IV.
SiO ₂	35.30	43.67	44.08	49.26
TiO ₂	1.20	—	—	—
SnO ₂	0.16	—	—	0.06
Al ₂ O ₃	22.62	36.69	36.84	25.26
Fe ₂ O ₃	5.68	2.10	0.48	—
FeO.....	18.04	0.55	0.74	0.84
MnO.....	1.19	trace	0.25	0.85
MgO.....	3.69	—	CaO = 0.21	—
(K,Rb,Cs) ₂ O....	8.60	8.57	11.10	13.85
Na ₂ O.....	0.62	1.95	0.20	0.35
Li ₂ O.....	0.30	trace	0.37	5.38
H ₂ O.....	1.21	4.35	4.98	1.76
Aq.....	2.30	1.15	1.17	—
F.....	0.60	0.35	0.19	5.68
<hr/>				
Total.....	101.51	99.38	100.61	103.29
Less O.....	0.25	0.14	0.08	2.38
<hr/>				
Total.....	101.26	99.24	100.53	100.91

I. Black lepidomelane; sp. gr. 3.0826; formula, $H_2R'_4R''_6R'''_8Si_{10}O_{41}$. II. Tombac-brown muscovite from the first zone; sp. gr. 2.8349; formula almost exactly that of damourite. III. Yellowish-white muscovite from the second zone; sp. gr. 2.8540. This analysis is in accord with that of the muscovite of Auburn, given by Clarke (Abstr., 1887, 347). IV. Lithionite from the third zone; sp. gr. 2.8245; formula, $(HO,F)_6R'_8Al_6Si_{10}O_{30}$. This formula differs from that given by Clarke and by Groth, in that the author's formula presents an excess of R'_2SiO_3 . A consideration of the various recent analyses of lepidolite indicates that the lithium micas form a continuous series, the members of which may be regarded as isomorphic mixtures of two terminal members. The author suggests that these terminal members are the pure muscovite silicate $R'_6Al_6Si_6O_{24}$, and the silicate



for which the name lithionite silicate is proposed. In the analyses given, the substance was dried at 100°, and in calculating the formula the water given off at 300°, indicated as Aq, was disregarded.

B. H. B.

Schorlomite, a Variety of Melanite. By G. A. KÖNIG (*Zeit. Kryst. Min.*, **13**, 650, from *Proc. Acad. Nat. Sc. Philad.*, 1886, 355).—Melanite, from California, containing titanium, and occurring as black masses in a greenish-yellow matrix, gave on analysis the following results (I):—

	SiO ₂ .	TiO ₂ .	Ti ₂ O ₃ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	CO ₂ .	MnO.	Total.
I.	30·71	4·47	3·29	2·26	22·67	32·41	0·30	3·36	—	99·47
II.	25·80	12·46	4·44	1·00	23·20	31·40	1·22	—	0·46	99·98

For comparison, the results (II) are given of an analysis of black schorlomite from Magnet Cove, Arkansas. The ratio of the constituents of the melanite (I) and of the schorlomite (II) is:—

(SiTi)O ₂ :	(FeTiAl) ₂ O ₃ :	(CaMgMn)O.	
3·03 :	1 :	3·10	(I)
3·16 :	1 :	3·22	(II)

These results appear to support the theory that schorlomite is a garnet in which titanium, in the form of Ti₂O₃, is substituted for aluminium.

B. H. B.

Tin-ore Deposits of Mount Bischoff. By A. v. GRODDECK (*Zeit. Kryst. Min.*, **13**, 636, from *Zeit. deutsch. geol. Ges.*, **38**, 370).—The author comes to the conclusion that, like the topaz rock of the Schneckenstein in Saxony, the rock of the tin-ore district of Mount Bischoff in Tasmania is a quartz porphyry converted into topaz. This alteration probably occurred during the formation of the tin-ore deposits. This theory is supported by the discovery of pseudomorphs of topaz after quartz. The interior of the crystals consisted of colourless quartz, whilst the exterior consisted of a dull white massive envelope of topaz, which gave on analysis the following results:—

SiO ₂ .	Al ₂ O ₃ .	F.	CaO.	SnO ₂ .	Total.
56·32	35·91	10·68	0·03	2·42	105·36

or, in other words, 63·21 per cent. of topaz, 35·39 per cent. of quartz, and 2·42 per cent. of tin oxide (compare Abstr., 1886, 603).

B. H. B.

Volcanic Blocks of Monte Somma. By B. MIERISCH (*Zeit. Kryst. Min.*, **13**, 627—628, from *Tschermak's min. Mitth.*, **8**, 113).—In the cavities of blocks of altered limestone, the author found grains of a colourless mineral hitherto supposed to be quartz. Analysis gave the following results:—

SiO ₂ .	MgO.	FeO.	Na ₂ O.	K ₂ O.	Ignition.	Total.
41·85	56·17	1·07	0·12	0·40	0·19	99·80

The mineral is obviously forsterite. It occurs in association with spinell and calcite. The occurrence of a silicate free from lime in a limestone block is remarkable.

In silicate blocks, especially in one composed principally of augite

and melilite, the author found a colourless mineral occurring in thin acicular crystals. It belongs to the nepheline group. It is optically monaxial, negative, exhibits basal cleavage, is very brittle, and has a sp. gr. of 2·602. Analysis gave the following results:—

SiO ₂ .	Al ₂ O ₃ + Fe ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	Total.
37·44	32·43	2·18	27·20	2·26	101·51

The mineral is thus a potassium-nepheline, $K_2Al_2Si_2O_8$, for which the author proposes the name of *kaliophilite*. B. H. B.

Selenium in Meteoric Iron. By H. N. WARREN (*Chem. News*, 57, 16).—Results are given below of the analysis of specimens of meteoric iron: 1 and 2 from Bohumilitz; 3, Pallus iron; 4, Elbogen; 5 and 6, Atacama Desert. In the method employed, 10 grams of the roughly-powdered specimen is mixed with sufficient flowers of sulphur, and heated to redness in a tube in a current of oxygen, the products of combustion passing into a series of bulbs containing distilled water, where the selenious acid is reduced by the sulphurous acid. The solution with the selenium precipitate is heated at 27°, and ultimately the latter is dried in an air-bath and weighed. In each case, a blank experiment was made with the sulphur employed.

	1.	2.	3.	4.	5.	6.
Fe	90·10	94·51	95·04	88·20	70·01	86·52
Ni	6·54	2·54	3·20	8·20	20·02	10·52
Mn	0·12	—	0·12	0·23	—	—
Co	0·24	0·32	0·12	0·12	—	0·12
Cu	—	—	0·20	—	—	—
Se	0·23	0·05	0·04	0·06	0·08	0·05

D. A. L.

Water from the Tönnissteiner Medicinal Spring. By B. LEPSIUS (*Ber.*, 21, 552—556).—This water contains a large excess of carbonic acid, and has an alkaline chalybeate taste; on analysis, the following results were obtained, which, when compared with a

Grams per litre.	1887. Lepsius.	1868. Fresenius.	Grams per litre.	1887. Lepsius.	1868. Fresenius.
K ₂ SO ₄	0·07213	0·09900	CaCO ₃	0·28072	0·38275
Na ₂ SO ₄	0·15324	0·14763	MgCO ₃	0·79622	1·07426
NaI	0·00004	0·00001	FeCO ₃	0·02908	0·02138
NaCl	1·40236	1·41489	MnCO ₃	0·00015	0·00031
NaBr	0·00064	0·00080	SiO ₂	0·02461	0·02741
NaNO ₃	0·00071	0·00046	B ₂ O ₃	trace	trace
Na ₂ HPO ₄	0·00003	0·00018	NaF	"	"
Al ₂ (PO ₄) ₃	0·00017	0·00013			
Li ₂ CO ₃	0·00303	0·00390	Total solids	4·51335	4·99855
Na ₂ CO ₃	1·74564	1·81999	CO ₂ { half combined	1·30119	1·49961
(NH ₄) ₂ CO ₃	0·00452	0·00533	CO ₂ { free	2·79929	2·39334
BaCO ₃	0·00001	0·00006			
SrCO ₃	0·00005	0·00006	Total	8·61383	8·89150

former analysis by Fresenius, show that the composition has remained practically unaltered for the last 20 years.

F. S. K.

Organic Chemistry.

Decomposition of Petroleum by Heat. By K. LISSENKO (*Dingl. polyt. J.*, **266**, 226, from *J. Berg u. Huttenwesens*, 1887, 349).—When petroleum is subjected to distillation, it is not only split up into constituents having different boiling points, but the high boiling products are decomposed into those of a lower boiling point. The yield of the latter increases with the time of heating, and in this manner the quantity of kerosine from Caucasian petroleum, which usually does not exceed 30 per cent., may be doubled. The best yield of kerosene is obtained from petroleum residues at a temperature of 434° to 501°. Nobel, however, found that the decomposition of the residues is best effected at 400°.

D. B.

Action of Bromine on Iodoform. By K. LÖSCHER (*Ber.*, **21**, 410).—By the action of bromine on iodoform, bromoform alone is obtained, and this, whether the bromine is employed in small quantity or in excess. The substance described by Serullas (*Ann. Chim. Phys.* [2], **34**, 225, and **39**, 97), and by Bouchardat (*Annalen*, **22**, 233) as bromiodoform, is merely a solution of iodoform in bromoform.

A. J. G.

Action of Zinc Ethyl on Nitroethane. By J. KISSEL (*J. Russ. Chem. Soc.*, 1887, 109—113).—In order to test the accuracy of the view he formerly expressed, that nitroethane is a compound of the constitution $\text{CH}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$ (*Abstr.*, 1885, 364), the author has studied the action of zinc ethyl on nitroethane. After several days' action at 0° in a sealed tube the mixture becomes solid, and when the tube is opened an inflammable mixture of gases escapes which is free from ethylene. The contents of the tube consist of a mixture of two compounds at least, of which one is crystalline and the other amorphous. The crystalline compound is decomposed by water containing a little sulphuric acid, and the nitroethane removed by evaporation, the liquid neutralised, and the zinc precipitated by sodium carbonate; on adding potash and distilling, a liquid boiling at 126—133° passes over. On neutralising this with hydrochloric acid, it yields the hydrochloride of a substituted hydroxylamine, $\text{NH}\cdot\text{Et}_2\text{O}\cdot\text{HCl}$. Another compound of similar composition is found among the numerous products formed in the reaction.

B. B.

Isobutylene Bromide and Bromotrimethyl Carbinol. By I. GUARESCHI and I. GARZINO (*Chem. Centr.*, 1887, 1343—1344, from *Ann. Chim. Farm.*, **87**, 101—112).—The moderately stable barium isobutylenedisulphonate, $\text{C}_4\text{H}_8(\text{SO}_3)_2\text{Ba} + 2\text{H}_2\text{O}$, was prepared by boiling 25 grams of isobutylene bromide with a saturated solution of

ammonium sulphite for 9 to 12 hours, then boiling with an excess of baryta-water, precipitating the uncombined barium with carbonic anhydride, and treating the concentrated filtrate with 95 per cent. alcohol. The free acid has not been crystallised. If the filtrate from this barium salt is evaporated to drive off the alcohol, and again treated with absolute alcohol, *barium γ -hydroxyisobutylenesulphonate*, $(\text{OH}\cdot\text{C}_4\text{H}_8\cdot\text{SO}_3)_2\text{Ba} + 1\frac{1}{2}\text{H}_2\text{O}$, and barium chloride separate. The formula $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$, has been given to the acid. The alcoholic filtrate from the last barium salt contains still another salt containing the same amount of barium. Isobutaldehyde is also formed by this reaction. If 30 grams of bromotrimethylmethane, CMe_3Br , is boiled with 150 c.c. of a saturated solution of ammonium sulphite, an inflammable gas (isobutylene?), trimethyl carbinol, boiling at $80\cdot5^\circ$ to $81\cdot5^\circ$, and trimethylmethanesulphonic acid are produced. By simply boiling the bromide with 3 parts of water, isobutane and trimethyl carbinol are formed.

When bromo- γ -isobutane is boiled for five hours with 5 parts of water, isobutaldehyde and *monobromotrimethyl carbinol*, $\text{CH}_2\text{Br}\cdot\text{CMe}_2\cdot\text{OH}$, are formed. The latter is a liquid boiling at $138\text{--}140^\circ$, of sp. gr. $1\cdot429$ at 0° , insoluble in water, but soluble in ether. J. P. L.

Compounds of Sodium Hydroxide and Methyl Alcohol.

By C. GÖRTIG (*Ber.*, **21**, 561—565).—When a methyl alcohol solution of soda is evaporated to a certain consistency, it solidifies to a crystalline mass on cooling; this compound, after drying, behaves similarly to those obtained from ethyl alcohol and soda or potash; namely, when agitated with water or some other liquids, it moves about on the surface, decomposes, and dissolves.

The composition of the compound formed varies with the conditions of its formation. (1.) If anhydrous methyl alcohol is employed and all moisture carefully excluded, the composition of the substance formed is $5\text{NaOH}\cdot 6\text{MeOH}$, when crystallisation is allowed to proceed slowly. (2.) When a little water is present, the composition is $\text{NaOH}\cdot\frac{1}{2}\text{H}_2\text{O}\cdot\text{MeOH}$. (3.) The composition varies when a considerable quantity of water is present, and seems to depend chiefly on the specific gravity of the solidifying solution, and on the relation between the quantities of water and alcohol.

Methyl alcohol also forms compounds with potash, and many other alcohols combine with potash and soda in a similar manner.

F. S. K.

Specific Gravities of Aqueous Glycerol Solutions. By W. W. J. NICOL (*Pharm. J. Trans.* [3], **18**, 302).—The following are determinations of the specific gravity at 20° of definite mixtures of glycerol and water :

Glycerol per cent.	Specific gravity.
100	1.26348
90	1.23720
80	1.21010
70	1.18293
60	1.15561
50	1.12831
40	1.10118
30	1.07469
20	1.04884
10	1.02391
Water at 20°	1.00000

A table calculated from these results for intermediate percentages is given in the paper. R. R.

Action of Boiling Acids on Methylenitan. By C. WEHMER and B. TOLLENS (*Annalen*, **243**, 334—342).—The authors maintain that the so-called formose which Loew obtained (this vol., p. 245) by the action of lime on formaldehyde is not a true carbohydrate, as it does not yield levulinic acid when heated with hydrochloric or sulphuric acid. W. C. W.

Levulose. By H. WINTER (*Chem. Centr.*, 1887, 1373—1374, from *Zeit. Rüb. Zuck. Ind.*, **24**, 796—820).—The specific rotatory power of a 20 per cent. solution of levulose is -71.4 at 20° . The discrepancies between the old and new values for the specific rotatory power of levulose cannot be attributed to the manner or source of production, inasmuch as they are found to have no influence.

Alcohol diminishes the rotatory power of levulose in a marked degree, but increases that of dextrose; the former phenomenon may probably be accounted for by the fact that levulose forms an alcoholate of the formula $C_6H_{11}EtO_8$. The specific rotatory power of anhydrous levulose in absolute alcohol is -47° for a concentration of 7.78 per cent.

As a mixture of equal parts of levulose and dextrose does not exhibit the optical properties of invert sugar, it is possible that the latter consists of four parts of levulose to three of dextrose. Levulose and dextrose in the proportion of two parts of the former to one of the latter form a well-defined crystalline product, which in solution exhibits no trace of birotation similar to that which exists in the case of a mechanical mixture in the same proportions. On account of the existence of this compound, a complete separation of the two sugars by means of alcohol is impossible.

An acetyl compound of levulose could not be obtained. Compounds of levulose with lime, lead oxide, chloride, and nitrate, iron and bismuth nitrate, were obtained. J. P. L.

Irisin. By O. WALLACH (*Ber.*, **21**, 396—397).—Ekstrand and Johanson recently described a carbohydrate from *Phleum pratense*,

to which they gave the name of graminin (see this vol., p. 246, also next Abstract). In the author's opinion, this is identical with irisin, the carbohydrate from *Iris pseudacorus* (Abstr., 1887, 526).

A. J. G.

Carbohydrates. By Å. G. EKSTRAND and C. J. JOHANSON (*Ber.*, **21**, 594—597).—The authors have found it necessary to modify some of the statements made in their last paper (this vol., p. 246), as it is now shown that they had confounded two carbohydrates under the name of graminin. To that which occurs in the haulm of *Phleum pratense*, and, mixed with another, in the rhizome of *Balldingera*, they give the name of *phlein*, reserving the name of graminin for a carbohydrate occurring much more widely diffused in the Gramineæ.

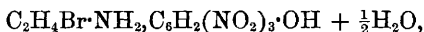
Graminin, $6C_6H_{10}O_5 + H_2O$, occurs in the rhizomes of *Trisetum alpestre*, *Agrostis*, *Calamagrostis*, *Festuca*, *Avena*, and in certain parts of *Balldingera*. It is lævorotatory; $[\alpha]_D = -38.89$; 100 parts of an aqueous solution at 9—10° contain 22.80 parts of graminin (dried at 100°); the sp. gr. of graminin dried at 100° is 1.522; it melts at 209°, and forms doubly refracting sphærocrystals.

Phlein: $[\alpha]_D = -48.12$ to -48.91 ; sp. gr. = 1.480; melting point 215°; 100 parts of the aqueous solution contain 3.26 parts of phlein (dried at 100°).

A. J. G.

Ethylamine-derivatives. By S. GABRIEL (*Ber.*, **21**, 566—575).—It has been found that bromethylphthalimide can be prepared by a more convenient method than that already described (Abstr., 1887, 1037), as the reaction between potassium phthalimide and ethylene bromide takes place considerably below 200°, and can be carried out in open vessels. This method is described in detail.

β-Bromethylamine hydrobromide, $C_2H_4Br \cdot NH_2 \cdot HBr$, is obtained by heating bromethylphthalimide with concentrated hydrobromic acid for two hours at 180—200° in sealed tubes. The product crystallises from alcohol in rhombic forms and melts at 155—160°; it is readily soluble in water, and when treated with concentrated potash yields an oil containing free bromethylamine. The *picrate*,



crystallises in amber-yellow prisms or needles which melt when placed in a capillary tube in boiling water, and gradually solidify again; the anhydrous salt melts at 130—131.5°. The *platinchloride*, which is tolerably soluble in water, forms orange-yellow scales.

When an aqueous solution of bromethylamine hydrobromide is boiled with silver carbonate, a product is obtained which crystallises from alcohol in flat, transparent forms, melts at 90—91°, and dissolves in water without alkaline reaction. This compound has the formula $C_2H_5NO_2$, and may be regarded as the anhydride of hydroxyethyl-carbamic acid, $OH \cdot CH_2 \cdot CH_2 \cdot NH \cdot COOH$.

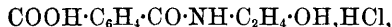
Bromethylphthalimide is decomposed by heating with sulphuric acid (1 pt. acid, 2 pts. H_2O); the filtrate from the phthalic acid yields three products. (1.) When the filtrate is freed from hydrobromic

2 g 2

acid and sulphuric acid and evaporated, a syrup is obtained, from which the addition of a considerable quantity of a 1 per cent. solution of picric acid precipitates a yellow, microcrystalline powder. This substance softens at 200° and melts at $205-210^{\circ}$. The mother-liquor yields on further evaporation slender, yellow, crystalline needles of *hydroxyethylamine picrate*, $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{NH}_2\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, which after recrystallisation from alcohol melts at 159.5° . (2.) If the filtrate is freed from sulphuric acid by adding barium carbonate and the excess of carbonate removed by careful addition of dilute sulphuric acid, a yellow, crystalline, hygroscopic mass is obtained on evaporation. This compound is *β -hydroxyethylamine hydrobromide*, $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{NH}_2\cdot\text{HBr}$; it crystallises in needles which melt below 100° , and its alcoholic solution gives with platinum chloride an oily platinumchloride which gradually becomes crystalline and is very soluble in water.

A very soluble acid compound is formed when bromethylphthalimide is treated with warm potash; after neutralising the free alkali with hydrochloric acid and evaporating the solution, a residue is obtained which, when heated at $130-150^{\circ}$ for about half an hour, is converted into *β -hydroxyethylphthalimide*, $\text{C}_8\text{H}_4\text{O}_2\text{N}\cdot\text{C}_2\text{H}_4\cdot\text{OH}$; this substance is only sparingly soluble, and crystallises from water in colourless needles or rhombic leaves; it melts at $126-127^{\circ}$ and is soluble in alcohol; it is insoluble in ammonia but gradually dissolves in potash.

The very soluble compound referred to above is probably *hydroxyethylphthalamic acid*; the *hydrochloride*,



was obtained in the form of colourless crystals melting at 85.5° . It dissolves in water, yielding an acid solution from which silver nitrate precipitates silver chloride. When boiled with silver carbonate, a colourless syrup is obtained which, on distillation, gives hydroxyethylphthalimide and water; the former distils above 360° , apparently not without decomposition, the crystalline distillate melting at $124-125^{\circ}$, and after crystallising from water at $126-127^{\circ}$. *β -Chlorethylamine hydrochloride*, $\text{C}_2\text{H}_4\text{Cl}\cdot\text{NH}_2\cdot\text{HCl}$, is formed when oxyethylphthalimide is heated with concentrated hydrochloric acid for three hours at $180-200^{\circ}$. On account of the extreme solubility of this salt in water, alcohol, and alcoholic ether, it could not be purified, but the *picrate*, $\text{C}_2\text{H}_4\text{Cl}\cdot\text{NH}_2\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7 + \frac{1}{2}\text{H}_2\text{O}$, was prepared. This salt crystallises in long, yellow needles, which lose water of crystallisation at 100° , and on heating quickly melt slightly above 100° . The anhydrous compound melts at $142-143^{\circ}$. The *platinchloride* crystallises in orange-coloured, microscopic, hexagonal plates, which dissolve readily in water, but only sparingly in alcohol or concentrated hydrochloric acid.

Chlorethylamine hydrochloride, when treated with potash, behaves in a manner similar to bromethylamine hydrobromide, but the free base seems to be more stable than the corresponding bromine-derivative.

Ethylene chloride acts on potassium phthalimide only at a much higher temperature than the bromide, and yields chiefly ethylenedi-

phthalimide. Ethylene chlorobromide and potassium phthalimide give a product consisting of chlorethyl- and bromethyl-phthalimide and ethylenediphthalimide; the mixture of the two haloïd compounds melts at 81—83°. F. S. K.

Ethylenimine (Spermine). By A. LADENBURG and J. ABEL (*Ber.*, **21**, 758—766).—When heated, ethylenediamine hydrochloride is partially converted into ethylenimine hydrochloride, the reaction being best effected by heating portions of 3 to 5 grams in small glass bulbs. The heating is stopped as soon as the contents have sublimed into the upper part of the bulb. The brown, carbonaceous mass is extracted with water, filtered, and the filtrate treated with a solution of potassio-bismuth iodide; the crystalline precipitate of the bismutho-iodide is then separated from an amorphous precipitate that falls at the same time. The yield is very small, the temperature at which ethylenediamine hydrochloride is converted into ethylenimine hydrochloride being above that at which the latter salt begins to decompose.

Ethylenimine, $\begin{smallmatrix} \text{CH} \\ < \\ \text{CH} \end{smallmatrix} \text{NH?}$, is prepared by distilling the bismutho-iodide with potash, evaporating on the water-bath, and drying under an exsiccator. The product so obtained, however, is not a base of low boiling point, as was expected, but a white, porcelain-like mass which deliquesces on exposure to air with absorption of water and carbonic anhydride. It melts at 159—163° in sealed tubes, can be sublimed, is insoluble in ether, readily soluble in absolute alcohol. The vapour-density is 2.93, corresponding with the doubled molecular formula $\begin{smallmatrix} \text{CH}\cdot\text{NH}\cdot\text{CH} \\ < \\ \text{CH}\cdot\text{NH}\cdot\text{CH} \end{smallmatrix}$. There seems some reason to think that the original distillate contains the base with the simple formula; it has a faint, piperidine-like odour which soon disappears, even when kept in closed vessels, and the readiness with which the base had passed over with the steam would seem to point in the same direction.

The *hydrochloride*, $\text{C}_2\text{H}_5\text{N}\cdot\text{HCl}$, crystallises in transparent tables, readily soluble in water, insoluble in alcohol. The *platinochloride*, $(\text{C}_2\text{H}_5\text{N})_2\cdot\text{H}_2\text{PtCl}_6$, forms small, well-formed, yellow prisms. The *aurochloride* crystallises in yellow, nacreous plates. The *picrate* forms small tables. The *mercurochloride* crystallises in feathery groups of needles. The *bismutho-iodide*, $3\text{C}_2\text{H}_5\text{NHI}\cdot 2\text{BiI}_3$, crystallises in lustrous, garnet-red plates, insoluble in cold, decomposed by boiling water.

Although the evidence is not yet absolutely conclusive, there seems strong reason to think that ethylenimine is identical with the base, spermine, obtained by Schreiner from human semen (*Abstr.*, 1879, 72). This point is still under investigation. A. J. G.

Action of Hydrogen Phosphide on Aldehydes and Ketonic Acids. By J. MESSINGER and C. ENGELS (*Ber.*, **21**, 326—336).—A slow, constant current of hydrogen phosphide can readily be obtained from phosphonium iodide by suspending it in ether (which must not be too moist for this purpose), and adding a few drops of water from time to time as the rate of evolution of the gas diminishes; 5 grams

of the iodide will in this way furnish a regular supply of gas for about an hour. It is best to work with small quantities of the iodide, and to add more as required. The gas is perfectly pure and free from iodine, is not spontaneously inflammable, and does not seem to be poisonous. The hydrogen iodide formed by the decomposition of the phosphonium iodide is wholly retained by the ether with the formation of a heavy, colourless oil which is insoluble in ether, has the composition $(\text{Et}_2\text{O})_2\text{HI}$, is decomposed by water with the formation of ether, hydriodic acid, and ethyl iodide, and on distillation yields first ether, then ethyl iodide, and finally hydriodic acid of the composition $2\text{HI} + 11\text{H}_2\text{O}$, boiling at 125° . Ether also forms a corresponding additive compound on treatment with hydrogen bromide.

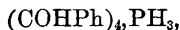
No absorption of the gas occurs under any conditions when a current of hydrogen phosphide alone is led through an aldehyde, but if at the same time hydrogen chloride is also passed through absorption takes place and is rendered more complete by adding ether to the aldehyde. The following compounds have been obtained from the corresponding aldehydes under these conditions.

Tetrahydroxyethylidenephosphonium chloride, $\text{P}(\text{CHMe}\cdot\text{OH})_4\text{Cl}$, crystallises in quadratic forms, melts at 112° , and is readily soluble in alcohol, insoluble in ether and carbon bisulphide. It has an unpleasant odour, is decomposed by water, and on treatment with aqueous potash is converted into Girard's tetrahydroxyethylidenephosphine and its hydroxide (Abstr., 1884, 1119). In addition to the chloride, an oil is also obtained, particularly when an excess of hydrogen chloride is passed into acetaldehyde, which seems to have the composition $[(\text{COHMe})_3\text{HCl}]_3\text{PH}_3$; it is readily soluble in alcohol, insoluble in ether, and decomposes on distillation. The corresponding bromine-derivatives were prepared by passing a current of hydrogen bromide together with hydrogen phosphide through acetaldehyde. The *bromide*, $\text{P}(\text{CHMe}\cdot\text{OH})_4\text{Br}$, crystallises in quadratic forms, melts at 88° , and deliquesces on exposure to the air. The oil, which is formed simultaneously, has the composition $[(\text{COHMe})_3\text{HBr}]_3\text{PH}_3$.

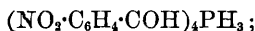
Tetrahydroxypropylidenephosphonium chloride, $\text{P}(\text{CHEt}\cdot\text{OH})_4\text{Cl}$, is crystalline, melts at 128° , and is readily soluble in alcohol, sparingly soluble in carbon bisulphide and chloroform, and insoluble in ether. It has an unpleasant, persistent odour, and is decomposed by water. The *bromide*, $\text{P}(\text{CHEt}\cdot\text{OH})_4\text{Br}$, crystallises in slender needles, melts at $105\text{--}106^\circ$, and closely resembles the chloride.

Isobutaldehyde and acraldehyde also absorb the gases, but the products were not obtained in the crystalline condition.

Benzaldehyde, under like conditions, yields a compound,



which crystallises in slender needles, melts at 153° , and is readily soluble in hot alcohol and chloroform, sparingly soluble in hot water, and insoluble in benzene, light petroleum, and carbon bisulphide. Metanitrobenzaldehyde forms an analogous compound,



cinnamaldehyde, under similar conditions, yields a crystalline com-

pound, which, however, is not homogeneous; salicylaldehyde does not form a crystallisable derivative.

When an ethereal solution of pyruvic acid is simultaneously treated with hydrogen phosphide and a rapid current of hydrogen chloride, a compound, $C_3H_5O_6P$, is obtained which crystallises in slender, silky needles, sublimes without melting, and is insoluble in ether, alcohol, chloroform, carbon bisulphide, and light petroleum, but readily soluble in ammonia and aqueous soda.

Acetone, ethyl acetate, and ethyl oxalate do not seem to react with hydrogen phosphide. The research is being continued.

W. P. W.

Amidoacetals. By A. WOHL (*Ber.*, **21**, 616—618).—*Amidoacetal*, $CH(OEt)_2 \cdot CH_2 \cdot NH_2$, is prepared by heating chloroacetal with alcoholic ammonia for 14 hours at $150-160^\circ$; the product is then mixed with sufficient baryta to decompose the chlorides, heated as long as ammonia comes off, and finally distilled with steam, when the primary base alone passes over. It is a colourless oil which shows the characteristic reactions both of a primary amine and an acetal. The *hydrochloride* is crystalline, very hygroscopic, and readily soluble in alcohol and alcohol-ether; the *platinochloride*, $(C_6H_{15}NO_2)_2 \cdot H_2PtCl_6$, crystallises in hexagonal forms. When an aqueous solution of the base is treated with excess of dilute sulphuric acid, and the liquid, after being made alkaline, is distilled with steam, a volatile base passes over; the aqueous solution of this base loses its alkalinity after a time, and on evaporation leaves a solid residue. Whether these substances are amidoaldehyde and the corresponding ketine will appear on further investigation.

An amido-compound is also obtained by the action of alcoholic ammonia on β -chloropropionacetal.

A. J. G.

Conversion of Ketoximes into Pseudonitroles. By R. SCHOLL (*Ber.*, **21**, 506—510).—Acetoxime (1 part) dissolved in ether (20 parts) is treated with rather less than the calculated amount of nitrogen peroxide, and the whole left until it has a deep blue colour and gives off no more gas. The product is washed with aqueous soda solution, then with water, dried with calcium chloride, and evaporated in a vacuum. Colourless crystals of propylpseudonitrole, $NO \cdot CMe_2 \cdot NO_2$, remain. The reaction seems to be capable of general application. Butylpseudonitrole was prepared from methylethylketoxime.

Diethylketoxime, $CEt_2 \cdot N \cdot OH$, is prepared by boiling diethylketone with a solution of hydroxylamine hydrochloride and soda in presence of alcohol for one to two hours; it is a colourless oil, boils at $162-163^\circ$ under 726 mm. pressure, and is insoluble in water.

Amylpseudonitrole, $NO \cdot CEt_2 \cdot NO_2$, obtained as above from diethylketoxime, forms large, tabular crystals, melting at 63° , and is soluble, with blue colour, in ether and chloroform.

An impure octylpseudonitrole is obtained in like manner from methylhexylketoxime. The latter boils at $213-214^\circ$.

N. H. M.

Tetrachlorinated Diacetyl. By S. LEVY and K. JEDLIČKA (*Ber.*, **21**, 318—321).—Experiments made by the authors show that the oily

product obtained by Stenhouse (this Journal, 1870, p. 8) by the action of chlorine in the presence of iodine on chloranilic acid is pentachloroacetone.

When chloranilic acid is treated with potassium chlorate and hydrochloric acid, noteworthy quantities of oxalic acid are formed together with a neutral brownish-yellow liquid which distils with partial decomposition at 180—196°. The distillate is a yellow oil, and consists of two substances, one of which (the chief product) is liquid, and the other a crystalline solid; the latter can be separated by crystallisation in a freezing mixture, and forms beautiful, yellow scales. The liquid product is purified by addition of water, which converts it into the crystalline *hydrate* of *symmetrical tetrachloroacetone*, $\text{CHCl}_2\cdot\text{CO}\cdot\text{CHCl}_2 + 4\text{H}_2\text{O}$. This crystallises from water in colourless, long prisms, melts at 48—49°, loses its water of crystallisation on further heating, and boils at 179—181° at 725 mm. pressure.

The coloured crystalline product is most probably *symmetrical tetrachloroacetyl*, $\text{CHCl}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{CHCl}_2$. It crystallises from ether in large, yellow tables, melts at 83—84°, and boils at 201—203° with slight decomposition at 740 mm. pressure yielding a yellowish-green vapour. It has a pungent odour, is soluble in water, alcohol, and ether, and is turned brown on treatment with aqueous soda and ammonia. Ammoniacal silver solution is not reduced by it, and no trace of red colour can be detected when it is added to a magenta solution decolorised by sulphurous anhydride. Finally, when treated with phenylhydrazine, it yields a very characteristic *phenylhydrazide*, which crystallises in slender, orange-red, woolly needles, melts at 186° with decomposition, and is very sparingly soluble in alcohol. The research is being continued.

W. P. W.

Thiocarbonyl Chloride. By H. BERGREEN (*Ber.*, **21**, 337—352).—The decomposition of thiocarbonyl chloride by water, which takes place very slowly in the cold, is complete at the end of a few hours on boiling. The products of the reaction are carbonic anhydride, hydrogen sulphide, and hydrogen chloride.

When dissolved in anhydrous ether free from alcohol, and saturated with carefully dried ammonia, thiocarbonyl chloride is converted into ammonium thiocyanate (compare Rathke, *Annalen*, **167**, 195), ammonium chloride, and a third substance which, however, could not be identified owing to the small quantity obtained. The thiamidoformic chloride, $\text{CSCl}\cdot\text{NH}_2$, which might possibly be regarded as an intermediate product of this reaction, was not formed by heating the chloride with ammonium chloride at 200° for some hours; on the contrary, complete decomposition occurred with the formation of carbon bisulphide and carbon tetrachloride. This result is due in some way to the presence of ammonium chloride, since thiocarbonyl chloride is decomposed only to a very slight extent when heated alone at 200° for a similar period.

Diphenylamine reacts with thiocarbonyl chloride in ethereal solution to form a compound which crystallises in small, pale-yellow needles, melts at 196°, and is probably identical with Bernthsen and Fries's tetraphenylthiocarbamide (*Abstr.*, 1882, 1089).

When thiocarbonyl chloride (5 grams), dissolved in benzene free from thiophen (25 grams), is treated with powdered aluminium chloride (8 to 10 grams) and the mixture heated on a water-bath for some time until hydrogen chloride ceases to be evolved, a compound is obtained whose composition approximates to that required for *thio-benzophenone*, CSPh_2 . This is a reddish-brown oil which dissolves readily in ether, benzene, and hot alcohol, and decomposes on distillation yielding a crystallisable distillate free from sulphur. When treated with hydroxylamine or with phenylhydrazine, it gives off hydrogen sulphide, and is converted into diphenylacetoxime or the phenylhydrazone of benzophenone respectively; hence it must be regarded as a thioketone. Behr (this Journal, 1873, 276) and Engler (Abstr., 1879, 61) have obtained compounds containing sulphur which have been described as thiobenzophenone; these substances, however, do not react either with hydroxylamine or phenylhydrazine, and cannot, therefore, be thioketones. The author suggests that Engler's compound (m. p. = 146.5°) may be a polymeride of thiobenzophenone corresponding with Wislicenus' thioduploacetone. Thiocarbonyl chloride also reacts with zinc methyl and zinc ethyl, and the compound obtained from the latter is a pungent, red oil, which can be distilled with steam. On analysis it was found to contain only four-fifths the amount of sulphur required for the formula CSEt_2 , and the non-crystallisable oil obtained, together with hydrogen sulphide, on treating its alcoholic solution with phenylhydrazine, yielded only one-half the nitrogen required for the formula $\text{CEt}_2\text{N}_2\text{PhH}$; these results are, however, attributed to the difficulty of purifying the compound, which most probably is *diethylthioketone*.

Ethyl chlorothioformate is obtained by the action of thiocarbonyl chloride (1 mol.) on an alcoholic solution of sodium ethoxide (1 mol.). The boiling point of this compound is probably $130-135^\circ$, but the specimen obtained boiled at $130-160^\circ$; its identity was, however, established by its conversion into xanthogenamide on treatment with aqueous ammonia. When 2 mols. of sodium ethoxide are employed, ethyl thiocarbonate is obtained (compare Klason, Abstr., 1887, 1029). The reaction with a solution of phenol in aqueous soda results in the formation of phenyl thiocarbonate, CS(OPh)_2 , which forms white, lustrous crystals, and melts at 97° .

The action of thiocarbonyl chloride on ketonic derivatives of the type of ethyl acetoacetate results in the displacement of both the hydrogen-atoms of the methylene-group by the thiocarbonyl radicle. Ethyl thiocarbonylacetacetate (CS:CAC:COOEt_2) (compare Norton and Oppenheim, *Ber.*, **10**, 703), for example, is obtained from ethyl sodacetoacetate and from ethyl cupracetoacetate; this compound does not react with phenylhydrazine or hydroxylamine, and probably is not a thioketone. An oil which could neither be crystallised nor distilled, and which contained sulphur but not chlorine, was formed when ethyl sodiomethacetoacetate in ethereal solution was treated with the chloride. Under like conditions, ethyl sodiomalonate yields the *thiocarbonyl*-derivative CS:C(COOEt)_2 , which crystallises in small, flesh-coloured needles, and melts at $177-178^\circ$. When this compound is saponified with alcoholic potash, and the product dis-

solved in water and treated with dilute sulphuric acid, hydrogen sulphide is evolved in small quantity, and a crystalline acid is obtained which cannot be recrystallised, since it decomposes partially on solution with the evolution of hydrogen sulphide. The analytical results are consequently only approximate, but they point to the formulæ CS:C(COOH)_2 for the acid, and CS:C(COOAg)_2 for the *silver* salt; the latter is pale-yellow in colour, and when touched with a small flame explodes like gunpowder, with the formation of silver sulphide, carbonic anhydride, and carbon. Thiocarbonyl chloride and ethyl sodiobenzoylacetate also react, forming *ethyl thiocarbonylbenzoylacetate*, $(\text{CS:CBz}\cdot\text{COOEt})_x$, which crystallises in yellowish needles, melts at $162\text{--}164^\circ$, and dissolves in sulphuric acid with a yellow colour. Lastly, the sodium compound of desoxybenzoïn is converted, under similar conditions, into the *thiocarbonyl*-derivative, $\text{C}_{15}\text{H}_{10}\text{OS}$, which crystallises in small, golden-yellow needles, melts at $285\text{--}286^\circ$, is much more sparingly soluble in ether, carbon bisulphide, light petroleum, and hot alcohol than the thiocarbonyl-derivatives of ethyl acetoacetate and ethyl malonate, and dissolves in concentrated sulphuric acid with a deep bluish-violet colour, recalling that of permanganate in solution.

W. P. W.

Calcium Copper Acetate. By F. RÜDORFF (*Ber.*, **21**, 279—281).—Calcium copper acetate, which was first prepared by Brewster (*Schweigger's Jahresh.*, **33**, 342), does not contain 8 mols. of H_2O , but has the composition $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 + 6\text{H}_2\text{O}$. The crystals are stable at the summer temperature and do not lose water of crystallisation when exposed over calcium chloride for 48 hours; decomposition, however, sets in at 60° . The salt cannot be recrystallised from water, and is not formed when solutions containing equimolecular proportions of its constituents are mixed together, since in both cases the resulting solution on cooling or on spontaneous evaporation yields crystals either of copper acetate or a mixture of the double salt and copper acetate until the solution contains the constituent salts in the ratio of 1 mol. of copper acetate to 3 mols. of calcium acetate; when this point is reached, crystals of the pure double salt begin to separate. The double salt can readily be prepared by dissolving 25 grams (1 mol.) of copper acetate and 66 grams (3 mols.) of calcium acetate in 350 c.c. of warm water; on cooling, the pure salt separates in quadratic forms, and the mother-liquor on concentration continues to yield pure crystals until 10 mols. of calcium acetate are present.

W. P. W.

$\beta\beta$ -Methylethylpropionic Acid. By P. v. ROMBURGH (*Rec. Trav. Chim.*, **6**, 150—156).—Secondary butylmalonic acid was prepared by heating ethyl sodiomalonate with secondary butyl iodide for several hours. The ethyl secondary butylmalonate obtained on fractionation of the crude product, is a colourless liquid of a pleasant odour; it boils at $233\text{--}234^\circ$ under a pressure of 774 mm.; sp. gr. at $75 = 0.988$. When heated with alcoholic potash, acidified with hydrochloric acid, and extracted with ether, it yields *secondary butylmalonic acid*, $\text{CHMeEt}\cdot\text{CH}(\text{COOH})_2$, which forms compact, transparent crystals

melting at 76° and becoming opaque in the air. It dissolves readily in water, ether, alcohol, and boiling benzene. With ammonium chloride and calcium chloride, it gives a precipitate almost insoluble in boiling water. The silver salt is white.

When secondary butylmalonic acid is gradually heated to 200° , it gives off carbonic anhydride, and yields $\beta\beta$ -methylethylpropionic acid, $\text{CHMeEt}\cdot\text{CH}_2\cdot\text{COOH}$, which boils at 196 – 198° under a pressure of 762 mm., and is optically inactive; sp. gr. at $15^{\circ} = 0.930$; vapour-density 3.99. The silver salt crystallises from hot water in curved needles; the calcium salt forms transparent needles which contain 3 mols. H_2O , and become opaque when exposed to dry air. The amide, prepared by Hofmann's method, forms long, transparent needles which melt at 124° , and can be sublimed without altering the melting point. It dissolves in warm water, in alcohol, ether, and boiling benzene.

The author concludes that $\beta\beta$ -methylethylpropionic acid has the same constitution as the caproic acid from the dextrogyrate hexyl alcohol obtained from Roman essence of camomile, but differs from it in being optically inactive. This alcohol would therefore have the constitution $\text{CHMeEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$. C. H. B.

Borneo Tallow. By A. C. GEITEL (*J. pr. Chem.* [2], 36, 515–518).—The author has examined an authentic sample of Borneo tallow (the produce of *Shorea stenoptera* and other dipterocarpons), from Java. It had a bright-green colour, which by long exposure to the air became at first yellow, and eventually white. At ordinary temperatures, it had the consistence of cacao-butter, which it somewhat resembled in taste and smell. It softened between the fingers, commenced to melt at 35 – 36° , and became perfectly fluid at 42° . On cooling, the oil did not solidify until the temperature had fallen considerably below the melting point. A portion of the tallow was saponified with potash, and the resulting soap decomposed with dilute sulphuric acid; the mixture of fatty acids thus obtained crystallised well, and, after repeated washings with warm water and careful drying, solidified at 54° . It consisted almost entirely of stearic and oleic acids, present in the ratio of two to one. The tallow contained about 10 per cent. of free stearic acid, and yielded a like quantity of glycerol. The author points out that the composition of Borneo tallow, and the ease with which it can be saponified, render it particularly well adapted to the manufacture of soap and candles.

G. T. M.

Action of Nitric Acid on Amides and Alkylamides. By A. P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 6, 140–149).—When nitric acid acts on amides and methylamides, it would seem that the radicle of the organic acid is displaced by that of nitric acid, or in other words, by NO_2 , but the amide of nitric acid is only stable when the two hydrogen atoms of the group NH_2 are displaced by a hydrocarbon radicle such as methyl. The three typical reactions may be represented by the equations: $\text{AcNH}_2 + \text{HNO}_3 = \text{AcOH} + \text{N}_2\text{O} + \text{H}_2\text{O}$; $\text{AcNHMe} + 2\text{HNO}_3 = \text{AcOH} + \text{MeNO}_3 + \text{N}_2\text{O} + \text{H}_2\text{O}$; and $\text{AcNMe}_2 + \text{HNO}_3 = \text{AcOH} + \text{Me}_2\text{N}\cdot\text{NO}_3$.

Heptylamide, prepared by Hofmann's method and treated with the strongest nitric acid, yields a volume of nitrous oxide corresponding with 1 mol. of the amide; acetylglycocine behaves in a similar way. All compounds containing acetyl are not attacked, but in the majority of cases when any reaction takes place, the acetyl-group is removed in the form of acetic acid, as in the case of the amides. The same reaction seems to take place with propane-derivatives.

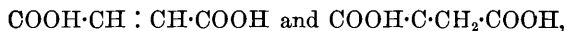
Strong sulphuric acid does not decompose the amides in the same way as nitric acid. In most cases the reaction in question does not occur between the free amides and nitric acid, but between the acid and nitrates of the amides which are first formed. It is possible that the nitric acid merely acts as a dehydrating agent, and this view would seem to be supported by the fact that sulphuric acid decomposes the nitrates of the amides in a precisely similar way. It is probable, however, that a sulphate is first formed, and the decomposition which ensues is due to the liberated nitric acid, and in fact if an amide is dissolved in sulphuric acid, there is no action beyond the formation of a sulphate, but on adding nitric acid decomposition at once begins. When the organic acid is not liberated, a stable nitro-derivative is formed, as in the case of dimethyloxamide. In other cases, a nitro-derivative may be formed in the first instance, but decomposes immediately. The action of acetic chloramide on silver nitrite yields acetic acid and nitrous oxide, a nitro-derivative possibly being formed as an unstable intermediate product.

Another possible supposition is that the action of nitric acid on nitrates of the amides is analogous to the formation of diazo-derivatives, and that unstable oxydiazocompounds are formed; thus, for instance, $\text{AcNH}_3\cdot\text{O}\cdot\text{NO}_2$ gives $\text{AcNH}(\text{O}\cdot\text{NO}_2) : \text{NO}\cdot\text{OH}$; these oxydiazoderivatives decomposing in accordance with the equations already given. This latter view is supported by the fact that a solution of dimethyloxamide in nitric acid evolves nitrous oxide after some time; that a solution of dinitrodimehyloxamide in nitric acid undergoes no change, and that if a solution of dimethyloxamide in nitric acid is poured into water immediately after its preparation, some little time elapses before the nitro-derivative separates.

No one supposition, however, is capable of explaining all cases. The main point is that the nature of the reaction is to a great extent determined by the nature of the acid radicle in the amide, and in some cases the nature of the alkyl radicles substituted in the NH_2 -group exerts a distinct influence, ethyl and methyl-derivatives not behaving in exactly the same way.

C. H. B.

Isomerism of Fumaric and Maleïc Acids. By R. ANSCHÜTZ (*Ber.*, **21**, 518—520).—Lossen (*Ber.*, **20**, 3310) suggests that the oxidation of fumaric and maleïc acids to tartaric and inactive tartaric acids may be explained with the help of the formulæ



usually ascribed to fumaric and maleïc acids respectively. In the present paper, the improbability is shown of inactive tartaric acid having

the constitution represented in the formula $\text{COOH}\cdot\text{C}(\text{OH})_2\cdot\text{CH}_2\cdot\text{COOH}$ (which would follow from the formula adopted for maleïc acid), on the ground that it does not react with phenylhydrazine, and further that the ethyl salt of inactive tartaric is very different in its behaviour to Wislicenus's ethyl oxalacetate, $\text{COOEt}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COOEt}$. Ethyl oxalacetate boils at 120° , and the ethyl salt of inactive tartaric acid at 156° (both under 14 mm. pressure). The latter salt still contains two hydroxyl-groups, and when saponified with lime-water yields the characteristic calcium salt of inactive tartaric acid.

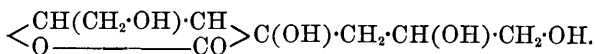
The only alternative formula for inactive tartaric acid is one in which two alcoholic hydroxyl-groups are represented as attached to two different carbon-atoms. The formation of an acid having this formula by the oxidation of maleïc acid, gives no support to the formula $\text{COOH}\cdot\text{C}\cdot\text{CH}_2\cdot\text{COOH}$ for the latter compound.

Having in view the observations of Brühl (Abstr., 1887, 1005) on the molecular refraction of aldehyde and paraldehyde, the author points out that differences in the molecular refraction of the ethyl salts of fumaric, maleïc, mesaconic and citraconic acids (Knops *Inaug. Diss.*, Bonn, 1887) harmonise with the formulæ for these compounds which he supports (compare also Abstr., 1887, 916). N. H. M.

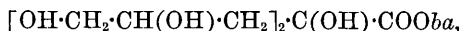
Oxidation of Diallyloxalic Acid. By P. BULITSCH (*J. Russ. Chem. Sec.*, 1887, 73—97).—The action of oxidising agents on diallyloxalic acid was investigated by Saytzeff and Schatzky, but formic, carbonic, and oxalic acids were the only products obtained. From the analogy of this acid to dimethyloxalic, diethyloxalic, and diisopropyloxalic acids, it might be inferred that on oxidation a ketone would first be formed, which would subsequently split up into acids with a lower number of carbon-atoms than the original acid. It also seemed desirable to ascertain whether citric acid is formed in the reaction, as was supposed by Schatzky.

In order to study the products of the limited oxidation of diallyloxalic acid, it was treated with very dilute nitric acid. For this purpose diallyloxalic acid (10 grams) was acted on by a mixture of nitric acid (65 grams) of sp. gr. 1.155 with an equal quantity of water, at as low a temperature as possible. When the action was complete, the greater part of the nitric acid was expelled by careful evaporation, and after removing the oxalic acid by means of barium carbonate, the filtrate was boiled with a strong solution of baryta. On cooling, a yellow barium salt separated; this, after being washed, was dissolved in aqueous acetic acid, precipitated hot with lead acetate, and the precipitate decomposed with hydrogen sulphide. The filtrate was concentrated and a mixture of alcohol and ether added to remove inorganic impurities. On evaporating the clear solution, a brownish or yellow syrup was obtained, which did not solidify at -20° , and could not be distilled with aqueous vapour without decomposition. It is insoluble in ether, chloroform, and carbon bisulphide, but easily soluble in alcohol or water. It reduces Fehling's solution on warming, but this may be due to some admixture; silver salts, however, are not reduced. Its reaction is feebly acid. Repeated analyses

point to the formula $C_8H_{14}O_6$, and its constitution, that of *tetrahydroxyoctolactone*, may be represented by the formula—



Of the metallic derivatives, the potassium, sodium, ammonium, lead and silver salts, could not be obtained in a state fit for investigation. By the action of barium or calcium carbonate at the ordinary temperature, the corresponding derivatives were obtained in the form of amorphous, gummy masses, which are easily powdered when dry. After drying in the desiccator, the derivatives have the formula $(C_8H_{15}O_7)_2Ba$ and $(C_8H_{15}O_7)_2Ca$, whereas on drying at 100° they lose 2 mols. H_2O , becoming $(C_8H_{13}O_6)_2Ba$ and $(C_8H_{13}O_6)_2Ca$ respectively. The constitution of the salts, dried at the ordinary temperature, is represented (where $ba = \frac{1}{2}Ba$), by the formula



the salt of a pentahydroxy-acid. After drying at 100° , the salt is only soluble in water with great difficulty, and no longer takes up the elements of water. On boiling the tetrahydroxyoctolactone with calcium or barium carbonates, basic salts are obtained, which, when dried in the desiccator, have the formulæ $C_8H_{16}O_8Ba$ and $C_8H_{16}O_8Ca$, and after drying at 100° become $C_8H_{12}O_6Ba$ and $C_8H_{12}O_6Ca$. The loss of 2 mols. H_2O is analogous to that mentioned in the first instance. When the lactone is boiled with aqueous baryta, a still more basic salt is obtained, having the formula $C_8H_{15}O_8ba_3$ (dried in the desiccator) and $C_8H_{13}O_7ba_3$ (dried at 100°). The calcium salt prepared in an analogous manner is, however, identical with that obtained with calcium carbonate (see above). The original lactone could be easily regenerated from the basic barium salt by transforming it into the lead salt, and decomposing the latter with hydrogen sulphide. Cold water is without action on tetrahydroxyoctolactone, but warm water dissolves it and the corresponding pentahydroxydipropylacetic acid seems to be formed. The lactone does not unite with iodine or hydrochloric acid, this being in accordance with the saturated character of the compound. The most careful oxidation with a very weak solution of potassium permanganate in alkaline solution (1 per cent.) yielded carbonic and oxalic acids only. B. B.

Action of Sulphuric Acid on Diallyloxalic Acid. By P. BULITSCH (*J. Russ. Chem. Soc.*, 1887, 97—106).—In order to study the hydration of diallyloxalic acid, and to compare the product obtained with tetrahydroxyoctolactone, the former was treated with sulphuric acid. For this purpose, sulphuric acid of $66^\circ B.$ is added drop by drop to diallyloxalic acid cooled with snow, when the mixture becomes brown, and some gas is evolved. The reaction is accelerated by warming the mixture gently from time to time, and cooling again immediately.

After addition of water, the liquid is boiled and saturated with barium hydroxide; the filtrate from the barium sulphate is then extracted with ether, which on evaporation leaves an oily liquid; this

is a mixture of a saturated with an unsaturated lactone, the latter being more easily soluble in ether than the former. In order to separate the two, the product obtained as above is boiled with water, and the unsaturated lactone taken up from the solution by extracting it twice (not more) with ether. After removing sulphuric acid from the aqueous solution by means of baryta and the excess of the latter by carbonic anhydride, the filtrate is concentrated by evaporation, and decomposed with sulphuric acid. The filtrate from the barium sulphate is again extracted with ether. The remaining liquid, containing the saturated lactone, is neutralised with lead carbonate, filtered, and after separating the lead in solution by hydrogen sulphide and precipitating the mineral salts with alcohol and ether, the saturated lactone is obtained. Its composition is $C_8H_{14}O_4$. It is a syrupy liquid, soluble in alcohol and ether, and having a feebly acid reaction, a bitter taste, and an agreeable odour, especially on gently warming. It does not reduce Fehling's solution. It forms an amorphous barium-derivative, $(C_8H_{15}O_5)_2Ba$, which does not lose water at 120° , and is the salt of a trihydroxy-acid.

The formula of the unsaturated lactone (which is much more soluble in ether than the saturated compound) is $C_8H_{12}O_3$, and it forms a barium-derivative, $(C_8H_{13}O_4)_2Ba$, not losing water at 120° , and a corresponding calcium-derivative. The saturated lactone is a dihydroxylactone, the unsaturated a monohydroxylactone.

When the saturated lactone, $C_8H_{14}O_4$, the product of hydration of diallyloxalic acid, is subjected to a further treatment with sulphuric acid, a dehydration takes place, the unsaturated lactone, $C_8H_{12}O_3$, being formed. The supposed structure of the lactones in question was confirmed by Hübel's test.

B. B.

Mucohydroxybromic and Mucohydroxychloric Acids. By H. B. HILL and A. W. PALMER (*Amer. Chem. J.*, 9, 147—174).—Reference is made to former work (*Abstr.*, 1879, 224; 1884, 731; 1885, 531) on the decomposition of mucobromic acid by baryta and by potassium phenoxide. The constitution of the mucohydroxybromic and mucohydroxychloric acids is represented by the formula



their bibasic characters being due to the environment of the hydroxyl-group; the aniline-derivatives are represented by the formula $COOH \cdot C(OH) : CX \cdot CH : NPh$, that is, as analogous to Böttlinger's anilglyoxylic acid (*Abstr.*, 1879, 51).

Mucohydroxybromic acid, $C_4H_3BrO_4$, is best obtained from mucobromic acid by very cautious treatment with baryta at a low temperature (yield 60 per cent.). The free acid is obtained by mixing the equivalent of sulphuric acid with the powdered barium salt, and evaporating in a vacuum. It is crystalline, melts at 111 — 112° , and its solution decomposes readily. The barium salt, $BaC_4HBrO_4 + 2H_2O$, is sparingly soluble in water, and decomposes readily when heated; an acid salt could not be obtained. The potassium salt, $K_2C_4HBrO_4 + H_2O$, and the silver salt, $Ag_2C_4HBrO_4$, are described, as well as the

dimethyl, diethyl, and monethyl salts, $C_4H_2BrO_4 \cdot Et$, only the last was obtained in crystals; it melts at $88-89^\circ$.

When the barium salt is boiled with baryta-water, carbonic, oxalic, formic, and hydrobromic acids are formed, together with an acid yielding a gummy barium salt.

The oxidation of mucohydroxybromic acid is best effected by bromine-water; oxalic acid, bromal hydrate, and hydrobromic acid are formed.

With phenylhydrazine or hydroxylamine, no definite compound with mucohydroxybromic acid could be obtained, but with the primary aromatic amines and carbamide crystalline condensation-products are readily formed.

Anilmucohydroxybromic acid, $C_4H_3BrO_3 \cdot NPh$, is most readily obtained by dissolving barium mucohydroxybromate in hydrochloric acid and adding aniline hydrochloride; it crystallises in pale-yellow needles, sparingly soluble in cold water, and melts at $131-132^\circ$. The salts $Ba(C_{10}H_7BrNO_3)_2 + \frac{1}{2}H_2O$, $K_2C_{10}H_6BrNO_3$, $Ag_2C_{10}H_6BrNO_3$, and a monobasic silver salt, are described; they are yellow and crystalline. With phenylhydrazine a crystalline compound,



is formed without elimination of water; it is very readily decomposed.

Mucohydroxychloric acid, $C_4H_3ClO_4$.—It has been previously shown that when treated with baryta, mucochloric acid yields α - β -dichloroacrylic and formic acids, but it is now shown that by adding the baryta only as fast as it is acted on, and at a low temperature, 73 per cent. of the theoretical yield of barium mucohydroxychloric acid is obtained, along with some α - β -dichloroacrylic acid. The free acid is obtained like the corresponding bromine compound; it is, however, more stable, and melts at $114-115^\circ$. The barium salt, $BaC_4HClO_4 + 2H_2O$, on keeping, changes to a more stable form, containing only 1 mol. H_2O ; the potassium and silver salts are anhydrous; the monethyl salt is crystalline, melting at $94-95^\circ$; but the diethyl salt is a viscous liquid. The barium salt, when heated with excess of baryta-water, is decomposed in just the same way as the mucohydroxybromic acid; there is no simple relation between the quantities of oxalic and carbonic acids formed. Bromine-water also decomposes the acid, just as it does the bromo-acid.

Anilmucohydroxychloric acid, $C_4H_3ClO_3 \cdot NPh$, is obtained in like manner to the corresponding bromine-compound; it contains 1 mol. H_2O , which is readily given off over sulphuric acid, or at 100° ; it is brilliant yellow, and melts with decomposition at $145-147^\circ$. The three salts, $Ba(C_{10}H_7ClNO_3)_2 + \frac{1}{2}H_2O$, $Ag_2C_{10}H_6ClNO_3$, and $K_2C_{10}H_6ClNO_3$, are described. With phenylhydrazine it forms a compound,



readily decomposed by acids or alkalis.

H. B.

Murexoin. By O. BRUNN (*Ber.*, **20**, 513—518).—Murexoin (Rochleder, *J. pr. Chem.*, **51**, 405) is prepared as follows:—Caffeine

is converted by Fischer's method (Abstr., 1882, 217) into dimethyl-alloxan, which is reduced by hydrogen sulphide to tetramethyl-alloxantin. This is finely powdered, and in portions of 5 grams moistened and spread on a plate, and exposed to the action of air and ammonia until the whole acquires a dark-brown colour. The murexoin is afterwards crystallised from hot water; the yield is almost quantitative. It is rather sparingly soluble in water with an intense colour resembling that of potassium permanganate, crystallises in slender prisms, and sublimes at about 230° without decomposition. When evaporated down with dilute hydrochloric acid, it decomposes into dimethylparabanic acid and another compound which could not be purified.

N. H. M.

Vapour-density of Aluminium Ethide. By L. ROUX and E. LOUISE (*Compt. rend.*, 106, 73—75).—The aluminium ethide was obtained by the action of mercuric ethide on aluminium in sealed tubes; it boiled at 195—200°. The vapour-density was determined by Meyer's method in an atmosphere of pure and dry nitrogen, the apparatus being heated by different liquids of known boiling points. The following results were obtained:—

Temperature	235°	258°	310°	350°
Vapour-density	8.1	6.2	2.5	2.5

It is evident that near its boiling point the vapour-density is normal, but at a higher temperature the compound dissociates, and the density is reduced to one-third. Most probably the compound splits up in accordance with the equation $\text{Al}_2\text{Et}_6 = 2\text{AlEt}_2 + \text{C}_4\text{H}_{10}$.

C. H. B.

Condensation of Furfuraldehyde with Chloraldehyde. By P. MEHNE (*Ber.*, 21, 423—428).—*Chlorofurfuracraldehyde*,



is prepared by slowly adding 10 per cent. aqueous soda to mixed aqueous solutions of furfuraldehyde and chloroacetaldehyde. It crystallises in broad, yellow, lustrous needles, melts at 79°, is soluble in hot water, ether, alcohol, benzene, light petroleum, and chloroform, and can be distilled with steam. The phenylhydrazine-derivative forms golden-yellow plates, begins to decompose at 142°, and melts at 157°. The *oxime* crystallises in small, white, interlaced needles, begins to sublime with decomposition at about 110°, and melts at 164—165°.

γ-Chlorofurfuracrylic acid, $\text{C}_4\text{H}_3\text{O} \cdot \text{CH} : \text{CCl} : \text{COOH}$, is prepared by heating the aldehyde with moist silver oxide for some days in a reflux apparatus; it crystallises in tufts of white needles, melts at about 142°, but sinters at a lower temperature. It is soluble in water, alcohol, ether, benzene, and chloroform, insoluble in light petroleum.

γ-Chlorofurfurpentic acid, $\text{C}_4\text{H}_3\text{O} \cdot \text{CH} : \text{CCl} : \text{CH} : \text{CH} : \text{COOH}$, is prepared by heating to boiling 4 parts of *γ*-chlorofurfuracraldehyde, 3 parts of anhydrous sodium acetate, and 5 parts of acetic anhydride, for three hours in a reflux apparatus. It forms clear yellow, interlaced needles, melts at 168°, and is soluble in alcohol, ether, benzene,

and chloroform, insoluble in light petroleum. With concentrated sulphuric acid, it gives a reddish-brown coloration, changing to reddish-violet.

A. J. G.

Polymerisation-products of the Tollyl Cyanates. By W. FRENTZEL (*Ber.*, **21**, 411—414).—*Diparatollyl dicyanate*, $C_2N_2O_2(C_7H_7)_2$, is obtained by the action of a few drops of triethylphosphine on tolyl cyanate; it melts at 185° with dissociation into the cyanate. Proof of the substance being the dicyanate is given by its reaction with absolute alcohol, which converts it into an allophanate; this crystallises in needles, and melts at 111° .

Paratollyl cyanurate, $C_3N_3O_3(C_7H_7)_3$, is prepared by heating the cyanate with potassium acetate at 100° for five hours; it forms white needles, and melts at 265° without decomposition.

Orthotollyl cyanurate is readily obtained by the action of potassium acetate on orthotollyl cyanate; it is white, crystalline, and suffers but slight decomposition on fusion. The corresponding dicyanate could not be obtained, the action of triethylphosphine on the cyanate only leading to a very partial polymerisation into the cyanurate.

A. J. G.

β -Nitrocymene. By A. F. HOLLEMAN (*Rec. Trav. Chim.*, **6**, 60—86).—20 grams of cymene is mixed with 200 grams of fuming nitric acid of sp. gr. 1.4, and the two layers of liquid are gradually mixed by passing a current of air into them, the temperature not rising above 50° . On pouring into water, a viscous, semi-solid mass is precipitated, which is separated by filtration through glass-wool by means of a pump. The crystals thus obtained are recrystallised from carbon bisulphide. They have the composition $C_9H_8NO_2$ (comp. Abstr., 1886, 1017), melt at 125° , and explode at about 160° in a vacuum. They dissolve readily in acetic acid and warm alcohol, in acetone, benzene, chloroform, carbon bisulphide, and ether, and are slightly soluble in cold alcohol and in boiling light petroleum. The compound separates from all the ordinary solvents in small, radiating needles. Its molecular weight as determined in acetic acid solution by Raoult's method is about 324, which agrees with the formula $C_{18}H_{16}N_2O_4$. With aqueous potash, it yields potassium paratoluate; with alcoholic potash, the products are ammonia, ethyl paratoluate boiling at 230 — 233° , and potassium paratoluate, but no hydrocyanic acid, cyanuric acid, nitrous or nitric acids. It follows that the nitrogen does not exist in the benzene-ring, and the methyl-group remains intact, and it would seem that the nitrogen has been substituted in the propyl side-chain of the cymene.

Sulphuric acid dissolves the so-called nitrocymene at 50° , and converts it into paratoluic acid. Sodium amalgam in warm alcoholic solution converts it into sodium paratoluate. Stannous chloride in presence of dilute alcohol produces hydrocyanic acid, ethyl paratoluate, and paratoluic acid.

If the nitrocymene is mixed with zinc-powder, added gradually to acetic acid, and the solution afterwards poured into water, a white or grey, flocculent precipitate is obtained, and if this is recrystallised from alcohol it yields small, pink needles of the composition $C_{18}H_{18}O_2$,

which melt at 159° , but cannot be sublimed. This compound is very slightly soluble in cold ethyl alcohol or light petroleum, somewhat soluble in boiling alcohol or benzene, insoluble in concentrated hydrochloric acid or in alkalis. This product of reduction differs from nitrocymene in containing H_2 in place of N_2O_2 , and it follows that the nitrogen does not exist in nitrocymene in the form of a nitroxyl-group. With acetic chloride, the product of reduction yields a substance of the composition $C_{18}H_{16}O$, which crystallises from alcohol in small, highly lustrous, white needles, melting at 164° . The acetic chloride acts as a dehydrating agent.

If the compound $C_{18}H_{18}O_2$ is dissolved in concentrated acetic acid and boiled with ammonium acetate, it yields bluish crystals of the composition $C_{18}H_{17}N$, melting at 197° . The action of ammonia is similar to that which it exerts on paradiketones, and the product may be regarded as *diparatolylpyrroline*. With hydrochloric acid, it yields a cherry-red resin soluble in alcohol, and with isatin it gives an intense red coloration after some days.

When heated at $170-180^{\circ}$ in sealed tubes for half an hour with an equal weight of phosphorus pentasulphide, the compound $C_{18}H_{18}O$ yields hydrogen sulphide and *diparatolylthiophen*, $C_{18}H_{16}S$, which crystallises in small, white plates melting at 171° . With isatin, it gives an intense dark-green coloration. The properties of the product of reduction, $C_{18}H_{18}O_2$, agree with those of diketones, and it probably has the constitution $C_6H_4Me \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot C_6H_4Me$.

If 100 grams of toluene and 30 grams of succinic chloride are added to 100 grams of aluminium chloride just covered with carbon bisulphide, and the product crystallised from acetic acid and from alcohol, small, reddish needles are obtained, identical with the product of reduction of β -nitrocymene. This result agrees with the constitution ascribed to the compound. Neither nitric nor nitrous acid converts it into β -nitrocymene.

β -Nitrocymene was treated with strong alcoholic ammonia, and the product evaporated to dryness on the water-bath and treated with ether. A white substance (A) remains undissolved, and some of the same substance is soluble in ether. The ethereal solution contains a second substance (B), which is insoluble in boiling benzene, whilst (A) is soluble; they can thus be separated. After purification by crystallisation from water or alcohol, the substance (A) forms colourless, rectangular crystals of paratoluamide, which melt at $158-159^{\circ}$, and are converted into paratoluic acid and ammonia by hydrochloric acid. This product is identical with paratoluamide prepared by heating ammonium paratoluate in sealed tubes at 230° . The product (B) seems to have the composition $C_{10}H_9N_3O_2$, melts at 162° , and is insoluble in acids and alkalis.

Hydrochloric acid in sealed tubes at 140° converts β -nitrocymene into ammonium chloride, paratoluic acid, carbonic anhydride, and carbonic oxide. The prolonged action of boiling hydrochloric acid produces paratoluic acid and hydroxylamine, with a small quantity of oxalic acid.

Paratolyl methyl ketone, prepared by Claus and Wollner's method, when carefully mixed with 10 times its weight of nitric acid of sp. gr. 1.4,

poured into water and the product crystallised from alcohol, yields small needles identical with β -nitrocymene. From this result it follows that β -nitrocymene contains two tolyl-groups. The presence of the group $C(NO_2) \cdot C(NO_2)$ is rendered probable by the formation of oxalic acid on treatment with hydrochloric acid, and the formation of carbonic anhydride and carbonic oxide when it is treated with the same acid in sealed tubes. The production of hydrocyanic acid on treatment with stannous chloride indicates that carbon is in direct union with the nitrogen, and the formation of ammonia and hydroxylamine points to the presence of the oximido-group. So-called β -nitrocymene therefore seems to be symmetrical *diparatolyldiisonitrosoethane*, $C_6H_4Me \cdot CO \cdot C(NO_2) \cdot C(NO_2) \cdot CO \cdot C_6H_4Me$.

With acetic anhydride, it yields rhombic crystals of the composition $C_{18}H_{14}N_2O_4Ac_2$ or $C_{18}H_{14}N_2O_4 \cdot Ac_2O$, which melt at 167° , and if introduced into concentrated sulphuric acid give a red coloration which disappears on adding water, and does not reappear on neutralisation. Water converts it into paratoluic acid, and hence it would seem that the acetyl-group has not really entered into combination.

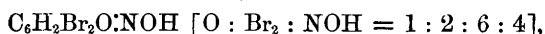
C. H. B.

Chlorophenols. By A. Mosso (*Chem. Centr.*, 1887, 1396; from *Ann. Chim. Farm.*, **87**, 184—191).—From equal molecular weights of metadichlorophenol and phthalic chloride, metadichlorophenyl phthalate, $C_6H_4(COO \cdot C_6H_3Cl_2)_2$, was obtained. It forms white needles melting at 108° . The *benzoate* forms white plates melting at 97° .

Orthochlorophenyl benzoate is a liquid which boils at 312 — 315° , and does not solidify below 0° ; the *phthalate* after crystallisation from alcohol melts at 98° . *Chlorophenyl benzoate* melts at 93° ; the *phthalate* melts at 11° . *Metachlorophenyl benzoate*? melts at 86° , and the *phthalate* at 108° .

J. P. L.

Dibromonitrosophenol. By O. FISCHER and E. HEPP (*Ber.*, **21**, 674—675).—*Diorthobromonitrosophenol*,



is prepared by the action of bromine on an alcoholic solution of nitrosophenol; it crystallises in small, lustrous plates, is readily soluble in alcohol and ether, more sparingly in chloroform and acetic acid, yields an amorphous potassium-derivative, and when reduced is converted into Hölz's diorthobromoparamidophenol. The statement previously made (*Abstr.*, 1887, 1105), that aniline converts the dibromo-derivative into a brominated azophenine, is incorrect; on further purification, all the bromine is removed and the product melts at 197 — 198° , and judging from its properties it is an oxyazophenine. The bromine in dibromonitrosophenol is very loosely combined.

A. J. G.

Benzyl Chloracetates. By K. SEUBERT (*Ber.*, **21**, 281—285).—To obtain these salts, a mixture of the calculated quantities of benzyl alcohol and the chloracetic acid, to which an excess of one of the constituents had been added, was allowed to remain for several days, then saturated with hydrogen chloride, and finally heated on a water-bath. The product, after washing with water and drying over calcium

chloride, was fractionated under reduced pressure in a Meyer's apparatus (Abstr., 1887, 884), and the distillate, after treatment with precipitated calcium carbonate to remove any acid present, was refractionated in a vacuum. Even under these conditions, a slight decomposition occurred. The products are colourless, strongly refractive liquids, insoluble in water, and readily soluble in alcohol and ether. The odour is strongly aromatic and persistent.

Benzyl chloracetate, $\text{CH}_2\text{Cl}\cdot\text{COOC}_7\text{H}_7$, boils at 147.5° at 9 mm., and has a sp. gr. = 1.2223 at $4^\circ/4^\circ$. Its refractive index $n_D = 1.5246$ at 18° (that of water being = 1.333), and its dispersion coefficient $\delta_n = 0.010272$. *Benzyl dichloracetate*, $\text{CHCl}_2\cdot\text{COOC}_7\text{H}_7$, boils at 179° at 60 mm., and has a sp. gr. = 1.313 at $4^\circ/4^\circ$. Its refractive index $n_D = 1.5268$ at 17.7° , and its dispersive coefficient $\delta_n = 0.010275$. *Benzyl trichloracetate*, $\text{CCl}_3\cdot\text{COOC}_7\text{H}_7$, boils at 178.5° at 50 mm. pressure, and has a sp. gr. = 1.3887 at $4^\circ/4^\circ$. Its refractive index $n_D = 1.5288$ at 18.8° , and its dispersion coefficient $\delta_n = 0.010191$. According to Persoz' rule, the calculated boiling points of the three compounds at the ordinary pressure are 269.5° , 275.5° , and 279.5° respectively. In the following table the calculated values of the specific and molecular refraction for each compound are obtained by regarding the three "double bonds" of the benzene nucleus as equivalent to six "single bonds."

Salt.	$M\left(\frac{n-1}{d}\right)$		$\frac{M}{d}\left(\frac{n^2-1}{n^2+2}\right)$	
	Found.	Calculated.	Found.	Calculated.
Benzyl chloracetate.	78.98	78.6	45.85	46.96
Difference	8.64	8.6	5.27	4.98
Benzyl dichloracetate.	87.62	87.2	51.12	51.94
Difference	8.63	8.6	5.00	4.98
Benzyl trichloracetate.	96.25	95.8	56.12	56.92

W. P. W.

Trimethoxybenzenes and the Constitution of Asarone. By W. WILL (*Ber.*, 21, 602—616).—1.3.5 *Trimethoxybenzene* (*phloroglucinol trimethyl ether*) is prepared by first passing hydrogen chloride into a solution of phloroglucinol in methyl alcohol, and then completely methylating the dimethyl ether so obtained with methyl iodide and potash. It forms colourless crystals, melts at 52.5° , boils at 255.5° (corr.) without decomposition, is insoluble in water and alkalis, readily soluble in alcohol, ether, and benzene. The *tribromo-derivative*, $\text{C}_6\text{Br}_3(\text{OMe})_3$, forms long, colourless needles, melts at 145° , and when treated with concentrated nitric acid, yields golden plates of the nitrate of a colourless base, which will be described later.

1:2:4 *Trimethoxybenzene* (*hydroxyquinol trimethyl ether*).—The method by which the ethyl compound was prepared by Will and Pukall (*Abstr.*, 1817, 660) did not prove successful with the methyl compound. The monomethyl ether of benzeneazoresorcinol was readily

obtained in dark-red needles melting at 114° , but such difficulty was experienced in converting this into the dimethyl ether (yellowish-red needles melting at 75°) that another method had to be adopted. Its preparation was at last effected by the methylation of methoxyquinol. 1 : 2 : 4 Trimethoxybenzene is a colourless oil which cannot be solidified in a freezing mixture, and boils at 247° (corr.). When treated with concentrated nitric acid, it yields a dinitro-derivative, forming brownish needles insoluble in cold water and dilute acids.

Methoxyquinone, $C_6H_3O_2 \cdot OMe$ [$OMe : O_2 = 1 : 3 : 6$], is obtained by oxidising orthanisidine with chromic mixture. It crystallises in slender, yellow needles, melts at 140° , sublimes readily, is sparingly soluble in water, readily in alcohol, very readily in alkalis, and yields an *anilide* when gently heated with aniline in acetic acid solution.

Methoxyquinol, $C_6H_3(OH) \cdot OMe$, is prepared by reducing the quinone with sulphurous acid. It forms colourless plates, melts at 84° , sublimes readily, and shows the properties characteristic of a quinol.

1 : 2 : 3 *Trimethoxybenzene* (*pyrogallol trimethyl ether*) is prepared by heating pyrogallol with excess of methyl iodide and potash dissolved in methyl alcohol, in a reflux apparatus. It crystallises in long, colourless needles, melts at 47° , and boils at 235° (corr.), is readily soluble in alcohol, ether, and benzene, insoluble in water and alkalis; the *tribromo*-derivative, $C_6Br_3(OMe)_3$, melts at 81.5° . When treated with concentrated nitric acid, it is converted into dimethoxyquinone and a nitro-derivative which forms thick prisms melting at 100° . A dinitro- and an amido-derivative were also prepared, melting at 126° and 114° respectively.

Dimethoxyquinone, $C_6H_2O_2(OMe)_2$, is separated from the accompanying nitro-ether by its sparing solubility in hot alcohol. It crystallises in thick prisms of golden lustre, melts at 249° , sublimes readily, and is sparingly soluble in hot water and ether, readily soluble in hot acetic acid. The *dibromo*-derivative forms yellowish-red, nacreous plates melting at 175° , and when reduced yields the corresponding dibromoquinol melting at 137° .

Dihydroxydimethoxybenzene is obtained by the action of sulphurous acid on the quinone. It forms lustrous, spear-shaped crystals, melts at 158° , dissolves in alkalis with green colour, and is reconverted into the quinone on oxidation.

Tetramethoxybenzene is obtained by the action of methyl iodide and potash on the preceding compound; it forms lustrous plates, melts at 47° , boils at 271° , and is readily soluble in alcohol, ether, benzene, and acetic acid, insoluble in water; the *dibromo*-derivative melts at 76° . When oxidised, it yields the dimethoxyquinone melting at 249° , together with another compound not yet investigated.

The trimethoxybenzene obtained from asarone is identical with the 1 : 2 : 4 trimethoxybenzene described above; it follows, therefore, that asarone has the constitution $C_3H_5 \cdot C_6H_2(OMe)_3$ [$C_3H_5 : (OMe)_3 = 1 : 3 : 4 : 6$]. (Compare next Abstract.) A. J. G.

Asarone. By B. RIZZA and A. BOUTLEROW (*J. Russ. Chem. Soc.*, 1887, 1—12).—In 1884 asarone was investigated by the authors (Abstr., 1884, 1042; 1885, 669), and found to be an unsaturated compound,

containing three methoxyl-groups. The molecular formula, $C_{12}H_{16}O_3$, was ascribed to it. On oxidation, it yielded a neutral, crystalline substance; this was subsequently investigated by Staats, and although his work confirms the authors' results in general, the sample which he analysed does not seem to have been pure.

In the present paper, the chemical nature of asarone is determined by the study of its products of oxidation, which are a neutral substance, an acid, and a compound derived from the latter by the elimination of a CO_2 group. Two methods are employed. In the first, the asarone (12 grams) is dissolved in strong acetic acid (40 grams) and potassium dichromate (6 grams) added; the mixture is then carefully heated until it turns green. On cooling and adding water, needle-shaped crystals separate together with a reddish-brown, resinous substance. The crystals are neutral, of a silky lustre, soluble in hot water, ether, light petroleum, and benzene. They melt at 114° , but sublime even at 100° . The analysis agrees with the formula $C_{10}H_{12}O_4$. Better results are obtained by the use of potassium permanganate solution (40 grams in 750 grams water), which is added drop by drop to a warm solution of asarone (10 grams in 450 grams water). The compound $C_{10}H_{12}O_4$ is extracted from the filtrate by means of ether; the alkaline solution is then evaporated to dryness, and the residue either extracted with hot alcohol or decomposed with hydrochloric acid, and then extracted with alcohol. In the first case the potassium salt of a new acid separates out from the hot spirit, in the second the new acid itself. Carbonic, formic, oxalic, and acetic acids are formed at the same time. When the operation is conducted as described, the quantity of acid formed is much larger than that of the neutral substance, but the reverse is the case when a mixture of asarone (5 grams) and finely-powdered permanganate (7.5 grams) is added in small portions at a time to boiling water. The acid, $C_{10}H_{12}O_5$, crystallises in needles, which are soluble in benzene, light petroleum, alcohol, and boiling water. It melts at 144° , and boils about 300° ; it has distinctly acid properties, decomposing carbonates. Its silver salt, prepared from the potassium salt, is tolerably stable under the influence of air and light.

The neutral substance, $C_{10}H_{12}O_4$, was found to be the aldehyde of the acid $C_{10}H_{12}O_5$, as was proved by the oxidising it with permanganate, when it was converted into the acid. Neither of these substances, however, has the properties of an unsaturated compound, so characteristically exhibited by asarone. That the neutral substance is an aldehyde is also proved by treating it with phenylhydrazine hydrochloride in the presence of sodium acetate, when yellow crystals are obtained, melting at 120 – 121° , and having the formula $C_{16}H_{18}O_3N_2$. By the action of sodium amalgam on the aldehyde, two new compounds are formed, one of which melts at 62° , the other at 102° . One of them seems to be the alcohol corresponding with the aldehyde, but they were not further investigated.

Three methoxyl-groups exist in asarone, and these are also present in the aldehyde and in the acid, as is shown by heating them with hydrochloric or hydrobromic acid, when methyl chloride or bromide is formed. It is best, however, to first heat the acid or aldehyde with four

times its weight of slaked lime, whereby it is converted into an oily substance of the formula $C_9H_{12}O_3$, boiling at $245-247^\circ$; this when heated with hydriodic acid in a sealed tube yields methyl iodide, corresponding in amount with three methoxyl-groups, from which it would appear that the constitution of this oil is $C_6H_3(OCH_3)_3$, that is, the trimethyl ether of a triatomic phenol. The presence of the benzene nucleus in asarone was proved by heating it with zinc-dust, and passing the products of distillation into strong nitric acid, when nitrobenzene was obtained.

The authors conclude from the study of the reactions of asarone and the allied compounds that their constitution may be expressed by the following formulæ: Asarone, $C_6H_2(OMe)_3 \cdot CH \cdot CH \cdot CH_3$; asarone dibromide, $C_6H_2(OMe)_3 \cdot CHBr \cdot CHBr \cdot CH_3$; the aldehyde, $C_6H_2(OMe)_3 \cdot CHO$; the acid, $C_6H_2(OMe)_3 \cdot COOH$, and the oily substance by $C_6H_3(OMe)_3$. Without regard to the position of the single group in the benzene nucleus, a striking analogy exists between asarone, the aldehyde, and the acid from asarone, and anethoil, $OMe \cdot C_6H_4 \cdot C_3H_5$, anisic aldehyde, $OMe \cdot C_6H_4 \cdot CHO$, and anisic acid, $OMe \cdot C_6H_4 \cdot COOH$, on one side, and eugenyl methyl ether, $(OMe)_2 \cdot C_6H_3 \cdot C_3H_5$, vanillyl methyl ether, $(OMe)_2 \cdot C_6H_3 \cdot CHO$, and veratric or dimethylresorcinic acid, $(OMe)_2 \cdot C_6H_3 \cdot COOH$, on the other. The authors consider it a complicated task to determine the relative positions of the substituting groups. The acid and the trimethyl ether were treated with phosphorus pentachloride, hydriodic acid, and, lastly, with hydrochloric acid, but only in the last case was a satisfactory result obtained. The product crystallised from hot water in glistening needles, melting about 250° , decomposition and sublimation taking place at a much lower temperature. It dissolves in sulphuric acid, forming a blue, and in nitric acid a green solution. With ferric chloride, the aqueous solution gives a black coloration, which in dilute solution becomes violet on adding a little sodium hydrogen carbonate. Its composition corresponds with the formula $C_{12}H_8O_4 = 2C_6H_3(OH)_3 - 2H_2O$, and it is to a certain degree analogous to phloroglucol. B. B.

Paranitrosoaniline. By O. FISCHER and E. HEPP (*Ber.*, **21**, 684—686).—The preparation and some of the properties of this substance have been already described (*Abstr.*, 1887, 1114). The sodium salt, $C_6H_6N_2O \cdot NaOH + H_2O$, prepared by mixing alcoholic solutions of the nitroso-compound and soda, is a yellow, crystalline mass. Paraphenylenediamine is formed when nitrosoaniline is reduced with tin and hydrochloric acid. With hydroxylamine hydrochloride in alcoholic solution, it yields Nietzki and Kehrmann's quinonedioxime (*Abstr.*, 1887, 575); this reaction seems common to all paranitroso-bases.

When nitrosoaniline is treated with phenylhydrazine hydrochloride, a compound, $C_{12}H_{14}N_4O$, is obtained, which crystallises in yellow needles, and when carefully heated melts at 125° with decomposition; when more quickly heated it explodes. Similar compounds with phenylhydrazine seem to be given by all nitroso-bases.

Nitrosoaniline when heated with aniline hydrochloride (1 part) and aniline (5 parts) yields the azophenine which Kimich obtained from nitrosophenol and nitrosodimethylaniline.

α -Nitroso- β -ethylnaphthylamine (Abstr., 1887, 1114) is also formed by the action of excess of a dilute aqueous solution of ethylamine on α -nitroso- β -naphthol. That this substance is really a secondary base is shown by its conversion into the corresponding nitrosamine, $C_{12}H_{11}N_3O_2$, when treated with nitrous acid; this crystallises in yellowish-white, woolly needles, gives Liebermann's reaction, and decomposes at 105° ; Ilinski's compound must be the primary base

of the formula $C_{10}H_6 \begin{array}{c} \text{N} \\ | \\ \text{NH}_2 \end{array} \text{O} \text{ [N : NH}_2 = 1 : 2 \text{]}.$

A. J. G.

Relation between the Constitution of Polybasic Unsaturated Organic Acids and the Formation of their Anilides. By A. MICHAEL and G. M. PALMER (*Amer. Chem. J.*, 9, 180—204).—The present means of distinguishing between acids of the maleic and fumaric series, depending on the formation of the anhydrides, is very unsatisfactory, as it necessitates the use of a high temperature, whereby intermolecular changes may occur, is extravagant with the material, and, moreover, is not applicable to a large number of unsaturated acids. Gottlieb has observed that an aqueous solution of aniline citraconate when boiled is converted into citraconanil, whilst a solution of aniline mesaconate suffers no change on evaporation; it is now found that this distinction is general between the acids of the fumaric and maleic series, as is shown by the following observations.

Maleic dianilide, $C_2H_4(CO \cdot NHPh)_2$, is formed when maleic anhydride, aniline, and water are heated together; it crystallises in long, white needles, melts at $211\text{--}212^\circ$, and is but sparingly soluble in cold water.

Maleic monanilide, $COOH \cdot CH : CH \cdot CO \cdot NHPh$, is formed by allowing a solution of the acid aniline salt to remain at ordinary temperature; it melts at 207° .

Aqueous fumaric acid and aniline may be heated together in any proportion without anything else than the aniline salt being formed.

Bromomaleic monanilide, $COOH \cdot CH : CBr \cdot CO \cdot NHPh$. Aqueous bromomaleic acid when treated in the cold with aniline yields first the acid aniline salt, $COOH \cdot CH : CBr \cdot COONH_3Ph$, melting at 128° ; the aqueous solution of this salt, if allowed to remain several days, deposits the anilide. If the treatment of the acid with aniline is effected with the aid of heat, entirely different products are formed; namely, a bright yellow substance, the anil of *phenylamidomaleic acid*, $\begin{array}{c} \text{NPh} \cdot \text{CO} \\ \diagdown \quad \diagup \\ \text{CO} \cdot \text{CH} \end{array} \text{C} \cdot \text{NHPh}$, melting at $229\text{--}230^\circ$, separates, and the mother-liquors deposit afterwards a lighter yellow substance, *phenylamidomaleic monanilide*, $COOH \cdot C(NHPh) : CH \cdot CONHPh$, which is soluble in very dilute potash, the anil being insoluble.

When cold aqueous bromofumaric acid is treated with aniline, the very insoluble acid aniline salt, $COOH \cdot CH : CBr \cdot COONH_3Ph$, melting at $153\text{--}154^\circ$, is formed. In contact with water or in solution, it does not change on keeping, but when boiled it deposits the yellow anil (m. p. $229\text{--}230^\circ$) just described.

Aqueous chlorofumaric acid and aniline easily yield the acid ammo-

nium salt, $\text{COOH}\cdot\text{CH}\cdot\text{CCl}\cdot\text{COONH}_3\text{Ph}$, soluble in alcohol, sparingly in water, and melting at 178° . Its aqueous solution, or the solid in contact in water, may be left any length of time without decomposition; but when the solution is boiled for some time it is converted into the yellow anil of phenylamidomaleic acid above described.

The acid aniline salt of dibromomaleic acid is easily prepared; being very sparingly soluble; when allowed to remain under water, an anilide is gradually formed, but not in a state of purity. The normal aniline salt also is insoluble, and is gradually converted into an anilide, $\text{NHPh}\cdot\text{CO}\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CO}\cdot\text{NHPh}$, melting at $138\text{--}140^\circ$, and when heated is converted into a yellow anil, $\langle \begin{smallmatrix} \text{CO}\cdot\text{CBr} \\ \text{NPh}\cdot\text{CO} \end{smallmatrix} \rangle \text{C}\cdot\text{NHPh}$, melting with decomposition at $182\text{--}183^\circ$.

The acid aniline salt of bromocitraconic acid,



melting at $120\text{--}121^\circ$, is readily converted under water or by heating with water into the anil, $\langle \begin{smallmatrix} \text{CO}\cdot\text{CMe} \\ \text{NPh}\cdot\text{CO} \end{smallmatrix} \rangle \text{CBr}$, melting at $144\cdot5\text{--}145\cdot5^\circ$.

Dianiline aconitate when boiled in aqueous solution yields an anilide, $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_3$, forming yellow needles melting at $250\text{--}252^\circ$, and a quantity of an amorphous substance; better results are obtained by allowing the solution to remain at ordinary temperatures, when an anilide, $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_4$, melting at $188\text{--}189^\circ$, is formed; hence it is clear that aconitic acid belongs to the maleic and not to the fumaric group.

Citraconic acid yields dimethylaniline and diethylaniline salts, which decompose readily on heating, but the formation of anilides has not been noticed. Itaconic acid behaves like citraconic acid with secondary and tertiary amines, but with aniline an anilide is formed. This difference may be made use of to separate primary from admixed secondary and tertiary amines.

Citraconic monanilide, $\text{COOH}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}\cdot\text{NHPh}$, is easily obtained by allowing a solution of monaniline citraconate to stand in the cold; it melts at 175° , and is soluble in alkalis, but is reprecipitated by hydrochloric acid. Dianiline citraconate does not change in aqueous solution until boiled, when the anil separates; this melts at 98° .

Itaconic monanilide, $\text{COOH}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)\cdot\text{CO}\cdot\text{NHPh}$, melts at 189° , and is obtained by boiling the acid with aniline and water, by allowing the solution of acid aniline itaconate to remain in the cold, as well as by Gottlieb's dry process.

Citracontolil, $\langle \begin{smallmatrix} \text{CMe}\cdot\text{CO} \\ \text{CH}\cdot\text{CO} \end{smallmatrix} \rangle \text{N}\cdot\text{C}_6\text{H}_4\text{Me}$, melts at $114\cdot5^\circ$, crystallises readily from hot water, and is insoluble in acids and alkalis. By warming the aqueous acid with paratoluidine, the acid toluidide, melting at 166° , is first formed; and by recrystallisation several times from hot water is converted into the tolil. Citraconic acid seems to form anilides with orthotoluidine and α - and β -naphthylamine. It is remarkable that such a feeble base as metamidobenzoic acid forms an anil, $\langle \begin{smallmatrix} \text{CMe}\cdot\text{CO} \\ \text{CH}\cdot\text{CO} \end{smallmatrix} \rangle \text{N}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, melting at 218° . Sulphanilic acid does

not react with citraconic acid, but phenylhydrazine readily yields an azide, $\langle \begin{smallmatrix} \text{CMe}\cdot\text{CO} \\ \text{CH}\cdot\text{CO} \end{smallmatrix} \rangle \text{N}_2\text{HPh}$, which forms bright yellow crystals, melting at 160° . Just as phthalic acid readily yields an anhydride, whilst its two isomerides do not, so also it yields an anil when its aniline salt is boiled with water or is allowed to stand, whilst the other two form aniline salts that are not so changed.

That the property of forming anilides on heating aqueous solutions of the aniline salts is characteristic of certain unsaturated acids, and is not shown by polybasic saturated fatty acids, is borne out by the negative results obtained from oxalic, malonic, succinic, tartaric, citric, camphoric, pyrotartaric, and mucic acids. H. B.

Nitrosotoluidines. By P. MEHNE (*Ber.*, **21**, 729—735).—*Nitroso-metatoluidine*, $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}$, $[\text{Me} : \text{NH} : \text{NO} = 1 : 3 : 6]$, is prepared by heating a mixture of 1 part of nitrosometacresol, 15 parts of dry ammonium acetate, and 5 parts of ammonium chloride with constant stirring on the water-bath for about half an hour, the reaction being facilitated by the addition of some powdered ammonium carbonate from time to time. It crystallises in glistening, steel-blue, feathery needles, which are green by transmitted light, melts at 178° , and is nearly insoluble in light petroleum, soluble in water, readily soluble in alcohol, ether, hot benzene, and chloroform. It dissolves in dilute acids with yellowish-red coloration, and when heated with alkalis is reconverted into nitrosocresol with evolution of ammonia.

Nitroso-orthotoluidine, $[\text{Me} : \text{NH} : \text{NO} = 1 : 2 : 5]$, is prepared from nitroso-orthocresol in like manner to the meta-compound. It crystallises in concentrically-grouped, globular aggregates of small, green needles with bluish reflex, and is very sparingly soluble in light petroleum, more readily in water, readily soluble in ether, alcohol, hot benzene, and chloroform. It is less stable than the meta-compound; when heated, it suffers slight decomposition at 60° , and melts at 115 — 116° with feeble explosion; when heated with aqueous soda, it yields ammonia and sodium nitrosophenol. When reduced with tin or zinc and hydrochloric acid, both nitrosotoluidines yield chlorinated products difficult to purify; these products were therefore oxidised with chromic acid, when in each case the same toluquinone (m. p. 70 — 71°) was obtained. This renders it very probable that in each the nitroso- and amido-groups are in the para-positions relatively to one another, further proof of this is obtained in the fact that both nitroso-compounds yield the same toluquinonedioxime when treated with hydroxylamine hydrochloride.

Toluquinonedioxime, $[\text{Me} : \text{NOH} : \text{NOH} = 1 : 2 : 5]$, so obtained forms small, yellow, microscopic needles, turns brown at 210° , explodes vigorously at 234° , and is soluble in hot water, alcohol, and ether, very sparingly in benzene and chloroform, insoluble in light petroleum. When oxidised in alkaline solution, it yields 2 : 5-dinitrosotoluene; this is yellow, noncrystalline, turns brown at 125° , melts with slight explosion at 144° , can be sublimed, and distils readily with steam. It is probable that the last two compounds are identical with those described by Nietzki and Guitermann (this vol., p. 471).

A. J. G.

Laws of Substitution of the Aromatic Amines. By L. LIMPACH (*Ber.*, **21**, 640—642).—In this and the following investigation of the laws governing the substitution of methyl for hydrogen in the benzene-ring in aromatic amines, the methylation was effected by heating the hydrochloride of the amine with methyl alcohol in molecular proportion at 250—300° under pressure.

Aniline yields mesidine, 1 : 3 : 4-metaxylylidine and paratoluidine, not even traces of either ortho- or meta-toluidine being ever observed. From this it follows that the methyl-group first takes the para-position to form paratoluidine, next by entering one of the ortho-positions, forms 1 : 3 : 4-metaxylylidine, and finally by occupying the other ortho-position yields mesidine.

Ortho- and para-toluidine both yield 1 : 3 : 4-metaxylylidine and mesidine. As shown by Hofmann, 1 : 3 : 4-metaxylylidine yields only mesidine. Further methylation in the benzene-ring could not be effected, the hydrogen-atoms standing in the meta-position relatively to the amido-group seeming to be incapable of being displaced by alkyl-groups. The statement of Nölting and Baumann (*Abstr.*, 1883, 893) as to the methylation of 1 : 3 : 4-metaxylylidine is incorrect.

A. J. G.

Methylation of Symmetrical Metaxylylidine. By L. LIMPACH (*Ber.*, **21**, 643—646).—The methylation was effected as described in the preceding Abstract. Symmetrical metaxylylidine yields isocumidine, $[\text{NH}_2 : (\text{Me})_3 = 1 : 3 : 4 : 5]$, which on further methylation yields Hofmann's pentamethylamidobenzene (*Abstr.*, 1885, 1128), and a new tetramethylamidobenzene; these can be separated by treatment with boiling water, in which the latter alone dissolves.

Tetramethylamidobenzene, $[\text{NH}_2 : (\text{Me})_4 = 1 : 2 : 3 : 4 : 5]$, crystallises in splendid, nacreous plates, melts at 66°, sublimes readily, boils at 259—260° (uncorr.), and then solidifies in large prisms which melt at 64°. The formyl compound crystallises in silky needles, and melts at 143—144°; the acetyl compound melts at 169.5°.

Tetramethylphenol, $\text{C}_6\text{HMe}_4\text{OH}$, prepared by mixing the sulphate of the base with a nitrite and heating, forms long, white needles, melts at 80—81°, boils at 248—250° (uncorr.), and can be distilled with steam.

Metatoluidine on methylation yields 1 : 2 : 4-orthoxylylidine. Paraxylylidine yields pseudocumidine, and this on further methylation yields the known tetramethylamidobenzene (m. p. 23—24°).

A. J. G.

Amides of Tribasic Fatty Acids. By A. SCHNEIDER (*Ber.*, **21**, 660—671).—When citric acid (1 mol.) and pseudocumidine (3 mols.) are heated for 12 hours at 160°, a mixture of tri- and di-cumidide are formed, and can be separated by boiling with alcohol, in which the dicumidide is the more soluble.

Citrotricumidide, $\text{C}_6\text{H}_5\text{O}_4(\text{NH}\cdot\text{C}_9\text{H}_{11})_3$, forms a white, microcrystalline powder, melts at 185°, and is sparingly soluble in alcohol, insoluble in water. When boiled with hydrochloric acid for some time, it is converted into cumidine and the dicumidide.

Citrodicumidide, $\text{C}_9\text{H}_{11}\cdot\text{N}\cdot\text{C}_6\text{H}_5\text{O}_4\cdot\text{NH}\cdot\text{C}_9\text{H}_{11}$, forms the main product in the reaction described above, but can be obtained free from the tri-

cumidide if only 2 mols. of pseudocumidine are employed. It crystallises in prisms, seemingly of the hexagonal system, melts at 173° , is insoluble in water and ether, readily soluble in alcohol, benzene, acetic acid, and chloroform. It is stable towards acids, but is converted by alkalis into *citrodicumidic acid*, $\text{COOH}\cdot\text{C}_6\text{H}_3\text{O}_3(\text{NH}\cdot\text{C}_6\text{H}_{11})_2$; this forms leafy crystals, melts at 194° , is insoluble in water, readily soluble in alcohol, benzene, and acetic acid. The sodium salt forms white needles, melts at $235\text{--}236^{\circ}$, and is very sparingly soluble in water.

Cumidine citrate, $\text{C}_6\text{H}_5\text{O}_7\cdot\text{C}_6\text{H}_{13}\text{N}$, is obtained by adding cumidine to a hot alcoholic solution of citric acid; it forms nodular crystals, melts at $132\text{--}133^{\circ}$, and does not yield citrocumidic acid when heated, but is resolved into its components.

Citrobenzidilic acid, $\text{C}_{12}\text{H}_8\langle\begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{smallmatrix}\rangle\text{C}_3\text{H}_4(\text{OH})\cdot\text{COOH}$, is prepared by heating an intimate mixture of citric acid and benzidine at $140\text{--}150^{\circ}$ for four to five hours. It forms a white, crystalline powder, which under the microscope seems to be rhombic, begins to decompose at 260° , and carbonises at above 300° without melting, is sparingly soluble in boiling alcohol, readily in acetic acid, and is insoluble in ether, benzene, light petroleum, chloroform, and carbon bisulphide. The salts are amorphous.

Normal benzidine citrate, $2\text{C}_6\text{H}_5\text{O}_7\cdot 3\text{C}_{12}\text{H}_{12}\text{N}_2$, is a white, amorphous powder, soluble in water, alcohol, and acetic acid.

Citrotolulylenediamide, $\text{C}_6\text{H}_5\text{O}_4\langle\begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix}\rangle\text{C}_7\text{H}_6$, is prepared by heating citric acid and tolulylenediamine (m. p. 99°) in molecular proportion for a day at $120\text{--}130^{\circ}$; it forms microscopic, seemingly octahedral crystals, decomposes at 187° , and can only be dissolved by very long-continued boiling with alcohol. *Normal tolulylenediamine citrate* was also prepared as a slightly yellow, amorphous powder. The action of ethylenediamine on citric acid led to no useful result.

Trinitrocitrotrianil, $\text{OH}\cdot\text{C}_3\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, prepared by nitrating Pebal's citrotrianil, forms yellow, rhombic crystals, melts at 108° with decomposition, and is soluble in ether, nitrobenzene, hot alcohol, and boiling benzene. When reduced, it is converted into aniline, and other products which could not be obtained in a pure state.

When sodium citrate is heated with cyanuric chloride, it yields sodium cyanurate and citric chloride.

Benzidine and aconitic acid do not react at moderate temperatures, whilst at higher temperatures, mixtures are formed of such a nature as to be unworkable.

Aconitotolulylenediamic acid, $\text{C}_7\text{H}_6\langle\begin{smallmatrix} \text{NH}\cdot\text{CO}\cdot\text{CH} \\ \text{NH}\text{---}\text{CO} \end{smallmatrix}\rangle\text{C}\cdot\text{CH}_2\cdot\text{COOH}$, is obtained by heating a mixture of tolulylenediamine and aconitic acid at $160\text{--}170^{\circ}$; it is a green, amorphous powder, which does not melt at 295° , is soluble in hot acetic acid, insoluble in water, alcohol, ether, and benzene, and soluble in alkalis.

Attempts to prepare the amides of aconitic acid were unsuccessful; the action of strong aqueous ammonia on ethyl citrate yields citrazinic acid.

A. J. G.

Aromatic Nitroso-bases. By L. WACKER (*Annalen*, **234**, 290—307).—*Paranitrosopropylaniline*, $\text{N} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{NHPr}^\alpha$, is prepared by the

action of alcoholic hydrogen chloride on the nitrosamine of normal propylaniline. It resembles nitrosoethylaniline in its properties, and forms steel-blue, needle-shaped crystals. It melts at 59° , and dissolves readily in alcohol, ether, and benzene. It forms crystalline salts with hydrochloric, sulphuric, oxalic, and picric acids. *Paranitrosopropylaniline-nitrosamine* melts at 69° , and dissolves in alcohol and ether. *Propylphenylenediamine* prepared from nitrosopropylaniline hydrochloride by reduction with tin and hydrochloric acid, boils at 281° without decomposition. It is soluble in alcohol, ether, and benzene, and forms a crystalline hydrochloride, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHPr}\cdot 2\text{HCl}$. By heating with aqueous soda, nitrosopropylaniline is decomposed into propylamine and nitrosophenol.

Paranitroso-isobutylaniline forms steel-blue crystals, melts at 93 — 94° , and forms a crystalline hydrochloride. The *nitrosamine* is soluble in alcohol, ether, and benzene. *Isobutylphenylenediamine* melts at 39° . The hydrochloride is soluble in water, but insoluble in ether. Nitroso-isobutylaniline is decomposed by boiling solutions of alkalis, yielding isobutylamine and nitrosophenol.

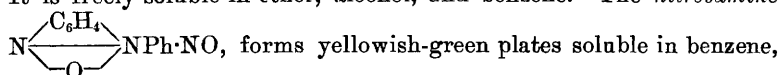
The preparation of nitroso- α -dinaphthylamine has been described by Fischer and Hepp (*Abstr.*, 1887, 729). By reducing the acid solution with tin, or the alcoholic solution with ammonium sulphide, amido- α -dinaphthylamine is obtained. The nitroso-compound is decomposed by boiling with dilute sulphuric acid into α -naphthylamine and α -nitrosonaphthol.

Nitrosophenyl- α -naphthylamine under similar treatment splits up into α -nitrosonaphthol and aniline. Reduction with tin and hydrochloric acid converts it into α -amidophenylnaphthylamine. This substance must have the constitution represented by the formula $\text{NHPh}\cdot\text{C}_{10}\text{H}_7\cdot\text{NH}_2$.
W. C. W.

Nitramine from Mesidine. By E. A. KLOBBIE (*Rec. Trav. Chim.*, **6**, 31—35).—Mesitylene was added gradually to cooled nitric acid of sp. gr. 1.5, and the small quantity of trinitro-derivative formed was separated by recrystallisation from boiling alcohol. A warm saturated alcoholic solution of the nitromesitylene was heated in sealed tubes at 110 — 115° with a concentrated aqueous solution of ammonium sulphide, and the nitromesidine was separated from the precipitated sulphur by solution in alcohol, from which it crystallises in yellow needles melting at 73° . When treated with nitrous acid, it yields mononitromesitylene. This was reduced by means of tin and hydrochloric acid, and the mesidine thus obtained was heated in sealed tubes at 220 — 230° for 48 hours with methyl alcohol and hydrochloric acid in the same proportions as in the preparation of dimethylorthotoluidine (*Abstr.*, 1879, 311). In this way, dimethylmesidine, boiling at 213 — 216° , is obtained, and this is dissolved in its own volume of concentrated sulphuric acid, added gradually to 10 or 12 times the weight of nitric acid of sp. gr. 1.5, boiled for a short

time, poured into cold water, and the precipitate crystallised from alcohol. The product forms yellowish, opaque crystals of the composition $C_{10}H_{12}N_4O_6$, very slightly soluble in cold alcohol. The two hydrogen-atoms in mesidine have been displaced by nitroxyl-groups, and the third nitroxyl-group must either have displaced methyl from the benzene nucleus, which is improbable, or have displaced one of the methyls in the amido-group. In that case, the product is *dinitromesitylene methylnitramide*, $C_6Me_3(NO_2)_2 \cdot NMeNO_2$. It melts at $137-138^\circ$, is easily soluble in benzene, ethyl acetate, and acetone, slightly soluble in ether and acetic acid, almost insoluble in light petroleum. With potash it yields no ammonia and no coloration, this result being due to the influence of the meta-position of the nitroxyl. Reduction with tin and hydrochloric acid does not yield satisfactory results; reduction with ammonium sulphide in sealed tubes at 120° yields yellow needles melting at 137° . C. H. B.

Paranitrosodiphenylamine. By M. IKUTA (*Annalen*, 243, 272—289).—The preparation and many of the properties of paranitrosodiphenylamine have been recently described by O. Fischer and Hepp (Abstr., 1887, 244). This substance dissolves in strong solutions of alkalis, forming salts which are decomposed by carbonic anhydride, the nitrosodiphenylamine being precipitated in a pure state. The picrate is deposited from an ethereal solution in crystals. It is decomposed by boiling with alcohol or ether. The base dissolves in acetic anhydride, yielding the *acetylamine* $NPhAc \cdot C_6H_4 \cdot NO$, a substance crystallising in red-coloured prisms and melting at $96-97^\circ$. It is freely soluble in ether, alcohol, and benzene. The *nitrosamine*



alcohol, and ether. It melts at 98° with decomposition, and yields Liebermann's reaction with phenol and sulphuric acid.

Paranitrosodiphenylamine is decomposed by boiling with alkalis or dilute sulphuric acid, yielding paranitrosophenol and aniline. It is completely reduced by alcoholic potash at 150° , or more easily by the action of tin and hydrochloric acid, forming *paramidodiphenylamine*. This amido-base melts at 66° and dissolves in ether and alcohol. The sulphate is crystalline and is almost insoluble in cold water. Ferric chloride produces in the aqueous solution of the hydrochloride a red coloration which changes to green.

Diazodiphenylamine sulphate forms golden needles. It is identical with the substance Fischer and Hepp obtained by treating paranitrosodiphenylamine with excess of sodium nitrite and dilute sulphuric acid. The relation between azophenine and nitrosodiphenylamine has already been discussed by Fischer and Hepp (Abstr., 1887, 1105).

The sulphate of diazodiphenylamine is converted into *parachlorodiphenylamine* by treatment with a 10 per cent. cuprous chloride solution. This is a feeble base. It melts at 74° , and dissolves freely in ether, alcohol, benzene, methyl alcohol, and light petroleum. The *nitrosamine*, $NO \cdot NPh \cdot C_6H_4Cl$, forms four-sided plates, melts at 88° , and dissolves freely in alcohol and ether. The ethereal solution

deposits crystals of paranitrosochlorodiphenylamine hydrochloride on the cautious addition of alcoholic hydrogen chloride.

Paranitrosochlorodiphenylamine melts at 158—159°, and crystallises in plates. It dissolves in alcohol, ether, chloroform, and benzene, also in sulphuric acid with a carmine coloration. When treated with aniline hydrochloride and aniline, it yields an azophenine-derivative melting at 230°.

W. C. W.

Action of Catechol on Alkylenediamines. By C. R1S (*Ber.*, 21, 378—386; compare Abstr., 1887, 722).—*Ethyleneorthophenylenediamine hydrochloride*, $2C_6H_{10}N_2 \cdot 3HCl$, crystallises in colourless, lustrous scales, melts at 150° with decomposition, and is readily soluble in water and alcohol. The *acetyl*-derivative, $C_8H_8N_2Ac_2$, crystallises in small, white granules, melts at 144°, boils with partial decomposition at 350° and is readily soluble in hot water, alcohol, benzene, and chloroform, sparingly soluble in ether at the boiling point. When heated with excess of methyl iodide and methyl alcohol for six hours at 100—110°, the base is converted into the *methiodide* of *dimethylethylene-orthophenylenediamine*, $C_8H_8N_2Me_2 \cdot MeI$, which crystallises from a dilute alcoholic solution in compact, colourless scales, melts above 200° with decomposition, is readily soluble in hot water and alcohol, sparingly soluble in benzene and ether, and is not decomposed by heating with aqueous soda or hydrochloric acid. On treatment in aqueous solution with silver oxide, it is converted into the ammonium-base, which forms a syrupy liquid having a strongly alkaline reaction, and yields a *platinochloride*,



crystallising in small, lustrous, yellow scales. If, however, ethylene-orthophenylenediamine is heated with methyl iodide alone at 100—110°, the *methyl*-derivative, $C_8H_8N_2Me$, is the sole product. It is a bright-yellow oil, which boils for the most part at 273—275°, is miscible with the ordinary organic solvents, and gives a pure blue colour on treatment with ferric chloride. This compound is also formed during the evaporation of the solution of the ammonium-base of the dimethyl-derivative, and can be obtained, together with ammonia, methylamine, carbon, and methyl iodide by the dry distillation of the corresponding methiodide.

Propylene-orthophenylenediamine, $C_6H_4 \langle \begin{smallmatrix} NH \\ NH \end{smallmatrix} \rangle C_2H_5 \cdot Me$, is formed when 1 gram of catechol is heated with 2.6 grams of propylenediamine at 200° for seven hours. It crystallises from light petroleum in colourless, lustrous scales, melts at 72°, boils at 283—284°, and is readily soluble in alcohol, benzene, chloroform, and hot water. The aqueous solution is coloured a pure blue by ferric chloride and the colour changes to green, yellowish-green, and finally reddish-brown on addition of much hydrochloric acid; the resulting solution, however, regains its original blue colour on boiling or on dilution with water. The *hydrochloride*, $2C_9H_{12}N_2 \cdot 3HCl$, is a pale rose-coloured, crystalline powder readily soluble in water and alcohol; the *picrate*, $3C_9H_{12}N_2 \cdot 2C_6H_3(NO_2)_3 \cdot OH$, crystallises in slender, sulphur-yellow

needles, decomposes at 160—161° with the evolution of gas, and is soluble in benzene.

W. P. W.

Aromatic Nitroso-bases. By E. KOCK (*Annalen*, **243**, 307—313).—*Ethylorthotoluylenediamine* is prepared by the reduction of the paranitroso-ethylorthotoluidine described by Fischer and Hepp (*Abstr.*, 1887, 244). It is a liquid boiling at 264 (corr.) and miscible with ether. The hydrochloride melts at 124° with decomposition; it is crystalline and deliquescent. *Paranitrosomethylorthotoluidine*, $C_8H_{10}N_2O$ (from orthotolylmethylnitrosamine), forms green plates. It melts at 151° and is decomposed by sodium hydroxide, yielding methylamine and paranitroso-orthocresol. Oxidation with potassium permanganate converts it into paranitromethylorthotoluidine. The nitro-product forms greenish-yellow needles and melts at 134°.

Paranitroso- α -naphthylethylamine dissolves in benzene, alcohol, and chloroform, and melts with decomposition at 133°. The hydrochloride, $C_{12}H_{12}N_2O \cdot HCl$, is sparingly soluble in dilute hydrochloric acid. The picrate melts with decomposition at 174°. The sodium salt, $C_{12}H_{13}N_2O_2Na$, forms white scales soluble in water and alcohol, forming orange-coloured liquids. The base is decomposed by sodium hydroxide into nitroso- α -naphthol and ethylamine, and by reduction with tin and hydrochloric acid is converted into *ethyl- α -naphthylenediamine hydrochloride*. This salt melts at 152°. The picrate melts at 180°, and is deposited from a hot aqueous solution in needles. The diamine has not been isolated.

W. C. W.

Relation between Hydrazides and Azo-compounds. By A. BERNTHSEN (*Ber.*, **21**, 743—745).—The author points out that the peculiar properties of the compound of phenylhydrazine with acridyl-aldehyde (*Abstr.*, 1887, 859) would seem to be due to another of those changes from hydrazines to azo-compounds to which attention was first called by the work of Japp and Klingemann (*Ber.*, **20**, 2942, 3284, 3398).

A. J. G.

Nitrocymene and Azocymene. By G. SHUMOFF (*J. Russ. Chem. Soc.*, 1887, 118—122).—Cymene, prepared partly by the action of phosphorus sulphide on camphor, partly from cumin oil, is dissolved in glacial acetic acid, and to the solution, cooled with ice and snow, a mixture of nitric acid of sp. gr. 1.52 is added. After addition of water, the nitrocymene is extracted with ether and reduced by means of sodium amalgam. The azocymene obtained in this way forms ruby-coloured plates, melts at 86°, is easily soluble in benzene, less so in alcohol. It is soluble without alteration in sulphuric and acetic acids, but insoluble in hydrochloric acid.

Zutkowsky finds that the crystals are rhombic: $a : b : c = 0.978284 : 1 : 1.567289$. The principal forms are the basic pyramid (111) and the pinacoid (001).

B. B.

Orthamidoazo-compounds of Xylene and Pseudocumene. By T. ZINCKE and H. JAENKE (*Ber.*, **21**, 540—548).—Orthamidoazo-

xylene can be diazotised in presence of excess of acid in alcoholic solution by nitrous acid or sodium nitrite.

The *hydrochloride* of the diazo-compound forms small, reddish-brown needles; the *nitrate* crystallises in wide needles rather sparingly soluble. The *sulphate* forms almost brick-red needles. When the salts are heated with alcohol, an azo-compound is formed identical with that obtained by oxidising the diazohydride. The *diazoperbromide*, $C_{16}H_{17}N_4Br_3$, crystallises in blood-coloured needles which melt with decomposition at $127-129^\circ$.

The *diazo-imide*, $C_{16}H_{17}N_5$, is prepared by the action of alcoholic ammonia on the dry perbromide in presence of much ether, and crystallises from light petroleum in stellate groups of thick, red needles readily soluble in ether; it melts at 77° , decomposes at 85° , and detonates when quickly heated.

The *diazohydride*, $C_{16}H_{18}N_4$, is obtained in a manner similar to the tolyl-compound. It forms small, yellowish, monoclinic prisms, melts at $136-137^\circ$, is insoluble in water, readily soluble in acetic acid and benzene, and in its behaviour resembles that of the diazohydride from orthamidazo-toluene (Abstr., 1886, 795). Nitric acid converts it into the diazo-nitrate, and silver oxide converts it into azoxylyene.

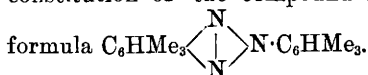
Metapara-azoxylyene, $C_{16}H_{18}N_2$ [Me : Me : N : N : Me = 1 : 2 : 4 : 5 : 1 : 3], is prepared from the diazo-salts of orthamido-azoxylyene or from the diazohydride. The yield is small and the purification difficult. It crystallises from alcohol in small, bright-red plates which melt at $46-47^\circ$, and is readily soluble.

When a cooled solution of orthamido-azoxylyene in 20 parts of glacial acetic acid is treated with an excess of a concentrated solution of potassium dichromate, and the solution, after some hours, precipitated with water, the compound $C_{16}H_{17}N_3$ is obtained. This crystallises in yellowish, monoclinic prisms melting at $83-85^\circ$. The compound is also formed when the diazoamide, $C_{15}H_{17}N_5$, is boiled in alcoholic solution.

The *diazo-compound* of orthamidopseudocumene is best prepared by passing nitrous anhydride into the solution of the latter compound in glacial acetic acid. The *perbromide* forms a dark-red crystalline precipitate melting at $122-124^\circ$ with decomposition. The *diazo-imide*, $C_{18}H_{21}N_5$, prepared from the perbromide crystallises in thick, red needles which melt at $90-91^\circ$ with decomposition and detonate when quickly heated. When the solution of the diazo-imide in glacial acetic acid is heated, the compound $C_{18}H_{21}N_3$ is formed.

The *diazo-hydride*, $C_{18}H_{22}N_4$, prepared by reducing the diazo-chloride with stannous chloride, crystallises from alcohol in small, lustrous, almost colourless, hexagonal plates melting at $151-153^\circ$; it dissolves rather readily in hot alcohol, glacial acetic acid and benzene, sparingly in ether and light petroleum. The compound $C_{18}H_{21}N_3$ is also formed when orthamidopseudocumene is dissolved in 20 parts of glacial acetic acid and a slight excess of concentrated solution of potassium dichromate added in drops. It is afterwards precipitated with water and crystallised from glacial acetic acid and then from methyl alcohol. It forms large, lustrous, whitish plates which melt at $83-85^\circ$. The

constitution of the compound is provisionally represented by the



N. H. M.

Quinonedioximes. By R. NIETZKI and A. L. GUITERMANN (*Ber.*, 21, 428—434; compare *Abstr.*, 1887, 575).—The most convenient method of preparing quinonedioxime (*loc. cit.*) is by the action of hydroxylamine on nitrosophenol. It crystallises in two modifications, probably differing in the amount of water they contain, namely, short, colourless needles, and long, slender, yellow needles which fall to a colourless powder on drying. Although, like all other paradioximes, it resembles the orthodioximes in general behaviour, yet it is sharply distinguished from the latter by its not forming an anhydro-compound; thus when heated with acetic anhydride it yields the diacetyl compound, $\text{C}_6\text{H}_4(\text{NOAc})_2$, which forms colourless needles and is sparingly soluble in water and ether, more readily in alcohol, very readily in acetic acid. The paradioximes and the dinitroso-compounds derived from them, when treated with concentrated nitric acid, are converted into the corresponding dinitro-derivatives; with quinonedioxime this furnishes the most convenient method of preparing paradinitrobenzene.

Toluquinonedioxime is best prepared by suspending nitroso-ortho-cresol in 50 to 60 parts of water, adding the calculated amount of hydroxylamine, and heating for 10 hours at $60\text{--}70^\circ$; it is also formed, although not so readily, from the meta-compound. It forms yellow needles, which become colourless on drying, explodes at 220° without melting, and on filtration becomes strongly electrical. The *diacetyl* compound crystallises in colourless needles, and melts at 120° . When oxidised with potassium ferricyanide in alkaline solution, it yields *dinitrosotoluene*; this compound, $\text{C}_7\text{H}_6(\text{NO})_2$, has only been obtained as an amorphous, yellow powder; is insoluble in all solvents except acetic acid, and is far more volatile than dinitrosobenzene; it sublimes markedly at 100° , and distils with steam—although with partial decomposition; it melts at 133° .

Paradinitrotoluene [$\text{Me} : \text{NO} : \text{NH} = 1 : 2 : 5$] is obtained by treating toluquinonedioxime or the dinitroso-compound with fuming nitric acid; it forms tufts of pale-yellow, moderately thick needles, and melts at 48° .

α -Naphthaquinonedioxime, $\text{C}_{10}\text{H}_6(\text{NOH})_2$, is prepared by suspending 5 grams of α -nitroso- α -naphthol in 500 c.c. of water, adding the necessary quantity of hydroxylamine hydrochloride and then so much alcohol that all dissolves on warming; the whole is then heated for two days in a reflux apparatus. It forms slender, colourless needles melting at 207° with decomposition, and yields an acetyl-derivative which crystallises in colourless, interlaced needles, and melts at 160° . It yields paradiamidonaphthalene on reduction, and, when oxidised with potassium ferricyanide in alkaline solution, is converted into 1:4-dinitrosonaphthalene; this forms a yellow, non-volatile powder, insoluble in all indifferent solvents; it explodes at 120° .

A. J. G.

Manufacture of Rosaniline by the Arsenic Acid Process. By O. MÜHLHÄUSER (*Dingl. polyt. J.*, **266**, 455—467, 503—517, and 547—563).—The preparation of rosaniline by heating aniline with arsenic acid was patented almost simultaneously by Medlock and Nicholson in 1860. In the same year Girard and de Laire patented the process in France, whilst, in 1864, Dawson obtained a patent according to which the dye was prepared by heating aniline under pressure with an aqueous solution of arsenic acid. The proportions of aniline and arsenic acid used by different manufacturers have varied very much; that now used which is found to give the best results is 1 mol. of arsenic acid, As_2O_5 , to 2 mols. of aniline. This mixture is heated in vertical cast-iron boilers provided with stirrers. The charge consists of 570 kilos. of syrupy arsenic acid of 74° B. and 340 kilos. of aniline oil of 1·008 sp. gr. It is heated gradually to about 120°, then more rapidly to 180°, after which the temperature is regulated so that the melt is finished during the next two hours, the final temperature being 185—189°. The crude melt contains the following ingredients:—Arsenious acid, arsenic acid, pararosaniline, methylpararosaniline, dimethylpararosaniline, chrysaniline, methylchrysaniline, violaniline, mauvaniline, brown colouring matters, and humus-like substances of unknown composition. Phenylated substances are formed when the quantity of aniline exceeds the proportion of 2 mols. to 1 mol. of arsenic acid. The oil mostly used has a sp. gr. of 1·008, distils between 190° and 198°, and is obtained by mixing 1 part of aniline with 2 parts of commercial toluidine. As the latter always contains 36 per cent. of paratoluidine and about 64 per cent. of orthotoluidine, the composition of the aniline oil is 33·3 per cent. of aniline, 24 per cent. of paratoluidine, and 42·7 per cent. of orthotoluidine.

The crude melt is allowed to cool, broken up roughly, and boiled up with water. The liquor is run into crystallising tanks in which it is treated with hydrochloric acid and salt. On standing, the crude rosaniline crystallises out; this is purified by recrystallisation. The different operations are described in detail in the original paper. The author also gives a minute account of the preparation of rosaniline base and of "cerise." He also discusses the working up of the crystallisation residues, the preparation of maroon, and the treatment of residues. D. B.

Azophenine and Quinonanilide. By O. FISCHER and E. HEPP (*Ber.*, **21**, 676—684).—The anilidoethoxyquinonanilide described by Zincke and v. Hagen (*Abstr.*, 1885, 787) is obtained when 1 part of azophenine is heated with 100 parts of alcohol and 5 parts of sulphuric acid for one hour at a temperature not exceeding 70°; it melts at 137°. If methyl alcohol is substituted for ethyl alcohol, the corresponding methoxy-compound, melting at 194°, is obtained. The melting points given by Zincke and v. Hagen are rather low.

When azophenine is boiled with stannous chloride and acetic acid, it is reduced to a colourless, crystalline substance, stable in acid solution, but converted by ammonia into a red base which yields blue salts.

Trichlorazophenine, $C_{30}H_{21}Cl_3N_4$, is prepared by adding 1 part of

nitrosodiphenylamine in small portions to a mixture of 1 part of parachloraniline hydrochloride and 5 parts of parachloraniline heated at 70° ; it forms brownish-red prisms, melts at 246° , and is soluble in alcohol. A different substance is obtained by the action of nitroso-phenol on parachloraniline; it forms red prisms, melts at 265° , is insoluble in alcohol, sparingly soluble in benzene, and, although not obtained quite pure, seems to be *tetrachlorazophenine*, $C_{30}H_{20}N_4Cl_4$.

By the action of nitroso-orthocresol on aniline, Zincke and v. Hagen's dianilidotoluquinonanilide (Abstr., 1883, 1118) is formed; it melts at $172-173^{\circ}$ (not 167°). *Diparatoluidotoluquinone-paratoluidide*, $C_{28}H_{28}N_3O$, is prepared in like manner from nitroso-orthocresol and paratoluidine; it crystallises in Bordeaux-red plates and melts at 191° .

The authors confirm Bröme's statement (this vol., p. 491) that all three nitroso-naphthols yield the same anilidoquinonanilide. This substance is also formed from benzeneazo- α -naphthol with aniline and aniline hydrochloride at 100° , from benzeneazo- α -naphthylamine, from nitroso-phenyl- α -naphthylamine, from benzeneazoethyl- α -naphthylamine, and from benzeneazophenyl- α -naphthylamine. In the last processes, a considerable quantity of a white, crystalline substance melting at 191° , of the formula $C_{34}H_{28}N_4$, but of unknown constitution is obtained; it is formed in smaller amount by the action of all nitroso-naphthols on aniline. Anilidonaphthaquinonanilide, from whatever source prepared, yields hydroxynaphthaquinone and aniline when heated with moderately concentrated sulphuric acid. When reduced with zinc-dust in acid solution, it gives aniline and naphthalene.

Dibromanilidonaphthaquinonanilide, $C_{22}H_{14}Br_2N_2O$, is prepared from α -nitroso- α - or β -naphthol by fusion with parabromaniline and parabromaniline hydrochloride; it forms long, red, interlaced needles, melts at 235° , and is very sparingly soluble in alcohol, more readily in benzene. The corresponding *dichloro*-compound melts at $217-218^{\circ}$.

On the whole, the authors consider that azophenine is better represented by the formula $C_{30}H_{24}N_4$ than by $C_{36}H_{28}N_5$, that proposed by Witt and adopted by the authors in their previous paper (Abstr., 1887, 1105). There can be no doubt of the intimate relation existing between azophenine and quinonanilide, and in confirmation of this it is now shown that if in preparing induline by heating quinonanilide with aniline and aniline hydrochloride at 170° , the experiment is stopped as soon as the melt begins to turn blue, azophenine is contained in the product.

A. J. G.

Action of Chloracetone on Diphenylthiocarbamide. By B. PAWLEWSKI (*Ber.*, **21**, 401-405).—*Acetonyldiphenylthiocarbamide*, $NHPh \cdot CS \cdot NPh \cdot CH_2 \cdot COMe$, is obtained, as its hydrochloride, by the action of chloracetone on diphenylthiocarbamide. It crystallises in long, pale-yellow prisms, melts at $139-140^{\circ}$ (uncorr.), resolidifies at $110-112^{\circ}$, and is insoluble in water, sparingly soluble in cold alcohol. The *hydrochloride*, $C_{16}H_{16}SN_2O \cdot HCl$, crystallises in long, quadratic needles and melts at $230-232^{\circ}$ (uncorr.); the *platinochloride*, $(C_{16}H_{16}SN_2O)_2 \cdot H_2PtCl_6$, is insoluble in water and alcohol.

Ethyl chlorocarbonate and thiocarbamide react to form a compound, $\text{NH}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{COOEt}, \text{HCl}$, which melts at 117° . Chloracetone and thiocarbamide yield a substance of the formula



melting at 126° . Similar reactions are being investigated.

A. J. G.

Substituted Biurets. By B. KÜHN and E. HENSCHER (*Ber.*, **21**, 504—506).—Triphenylbiuret is formed when diphenylcarbamide is dissolved in an excess of hot phenyl cyanate, and the whole heated for half to one hour at 150° ; at a higher temperature, it decomposes into diphenylcarbamide and phenyl cyanate. Diphenylbiuret prepared from monophenylcarbamide melts at 208 — 210° .

Phenylparaditolylbiuret, $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}_2$, melts at 140° .

Phenylbenzylparatolylbiuret, $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}_2$, crystallises from dilute alcohol in microscopic needles melting at 95 — 104° .

Paratritolylbiuret, $\text{C}_{23}\text{H}_{23}\text{N}_3\text{O}_2$, melts at 155 — 156° .

Orthoparaditolylbiuret, $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_4$, is prepared from paratolylcarbamide and paratolyl cyanate, and crystallises from dilute alcohol in white needles which melt between 216° and 224° .

Diphenylparatolylbiuret, $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_2$, melts at 214 — 216° .

N. H. M.

Derivatives of Ortho-xylene. By H. STRASSMANN (*Ber.*, **21**, 576—581).—*Ortho-xylylphthalimide*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{N}\cdot\text{C}_8\text{H}_4\text{O}_2$, is obtained by heating ortho-xylyl bromide and potassium phthalimide at 200° for half an hour; the product crystallises from alcohol in white, hexagonal forms, melting at 148 — 149° ; the yield is 76 per cent. of the theoretical amount.

Ortho-xylylphthalamide acid, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, is produced when the preceding compound is boiled with soda; it melts at 156° , and crystallises from alcohol in needles.

Ortho-xylylamine hydrochloride is formed when xylylphthalimide is heated in sealed tubes with hydrochloric acid; the product crystallises from alcohol in transparent needles, and when treated with alkalis yields *ortho-xylylamine*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{NH}_2$, which is a colourless liquid boiling at 202° . The *platinochloride*, $(\text{C}_6\text{H}_{11}\text{N})_2\text{H}_2\text{PtCl}_6$, crystallises in yellow needles, the *sulphate* in prisms, readily soluble in water, and the *picrate*, $\text{C}_6\text{H}_{11}\text{N}_3\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, in long, yellow needles, which decompose above 170° without melting.

Ortho-xylylthiocarbamide, $\text{NH}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, is obtained by dissolving equivalent weights of ortho-xylylamine hydrochloride and potassium thiocyanate, and heating the residue obtained on evaporation at 140° for some time. It crystallises from water in white needles, melting at 167° , and turning red on exposure to the air.

Ortho-xylylcarbamide, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, is prepared in a similar manner from the sulphate of the base and potassium cyanate; it crystallises from alcohol in radiating moss-like forms, melting at 172 — 173° .

Ortho-xylylacetamide, $\text{C}_6\text{H}_5\cdot\text{NHAc}$, is formed when the hydrochloride

is heated with sodium acetate and acetic anhydride; it crystallises from alcohol in needles melting at 69° .

Ortho-xylylthiocarbimide, $\text{CSN}\cdot\text{C}_6\text{H}_9$, is produced when an ethereal solution of the base is mixed with carbon bisulphide, and then distilled with mercuric chloride; it is an oil, boiling at 256° , and smelling strongly of radishes.

Ortho-xylylenediphtalimide, $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{O}_2)_2$, is obtained in almost theoretical quantities by gradually heating an intimate mixture of xylene bromide and potassium phthalimide to 200° ; it crystallises from acetic acid in slender, white needles melting at 253° .

Ortho-xylylenediamine hydrochloride is formed when the preceding compound is heated with hydrochloric acid at 200° for two hours; when treated with potash, it yields the free base.

Ortho-xylylenediamine, $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{NH}_2)_2$, is a strongly alkaline liquid with an ammoniacal smell, and attracts carbonic acid from the air; it gives a yellowish-red precipitate with ferric chloride, and yields the salt, $\text{C}_6\text{H}_4\text{N}_2\text{Au}_2\text{Cl}_6$, in yellow plates, when precipitated with auric chloride. The *picrate*, $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{NH}_2\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7)_2$, crystallises in yellow needles, which decompose above 170° without melting.

Orthodiacetylxylylenediamine, $\text{C}_6\text{H}_8(\text{NHAc})_2$, crystallises in tufts of needles and melts at 146° . *Orthodibenzoylxylylenediamine*,



obtained by heating the hydrochloride with benzoic chloride at 200° , crystallises in needles melting at 168° .

Chloro-xylylenephthalimide, $\text{CH}_2\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{O}_2$, is prepared by heating xylene chloride (1 mol.) with potassium phthalimide (1 mol.); it crystallises from alcohol in prisms, melting at 140° , and when heated with hydrochloric acid yields *chloro-xylylamine hydrochloride*, $\text{CH}_2\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HCl}$. F. S. K.

Tetrabenzylphosphonium - compounds. By B. LEDERMANN (*Ber.*, **21**, 405—409).—*Tetrabenzylphosphonium iodide*, $\text{P}(\text{C}_6\text{H}_5)_4\text{I}$, is prepared by heating phosphonium iodide (1 mol.) and benzyl alcohol (3 mols.) in sealed tubes at 100° for six to eight hours; it crystallises well, melts at 191° , and is sparingly soluble in water, more readily in chloroform, ether, and alcohol. The *chloride*, $\text{P}(\text{C}_6\text{H}_5)_4\text{Cl}$, prepared by digesting the iodide with silver chloride, forms white crystals. The *sulphate*, $(\text{PC}_{25}\text{H}_{25})_4\text{SO}_4$, also forms white crystals. The *platinochloride*, $(\text{PC}_{25}\text{H}_{25})_2\text{PtCl}_6$, is obtained as a yellow, crystalline precipitate. The *nitrate* and *bromide* both form white crystals. The *picrate* forms yellow crystals. The *mercuriochloride*, $\text{P}(\text{C}_6\text{H}_5)_4\text{HgCl}_3 + \text{H}_2\text{O}$, and *stannochloride*, $(\text{PC}_{25}\text{H}_{25})_4\text{SnCl}_6$, are insoluble. The hydroxide could not be formed, as moist silver oxide is without action on the haloïd salts, and the sulphate, when treated with barium hydroxide, yields tribenzylphosphine oxide. When tetrabenzylphosphonium iodide is boiled for some time with strong alkalis, tribenzylphosphine oxide and toluene are formed.

The oxygen in tribenzylphosphine oxide is so firmly combined that it is not displaced by treatment with phosphoric chloride or potassium

hydrosulphide. Experiments made with a view to isolate tribenzylphosphine were unsuccessful. A. J. G.

Conversion of Ketones and Aldehydes into Acids and Acid Amides by Means of Ammonium Sulphide. By C. WILLGERODT (*Ber.*, 21, 534—536).—The compounds formed by the action of ammonium sulphide on methyl aromatic ketones are not ketone-imides (Abstr., 1887, 1046) but acid amides, accompanied with the ammonium salts of the corresponding acids. Phenyl methyl ketone yielded phenylacetamide and phenylacetic acid; paratolyl methyl ketone, paratolylacetamide (m. p. 185°), and paratolylacetic acid (m. p. 92°), &c.

Aromatic ethyl and propyl ketones react similarly with ammonium sulphide. In the case of paratolyl ethyl ketone, the reaction takes place at 250°. From α -naphthyl ethyl ketone and α -naphthyl propyl ketone, the compounds $C_{13}H_{13}NO$ and $C_{14}H_{15}NO$, melting respectively at 140° (uncorr.) and at 160°, were obtained.

When benzil is heated with ammonium sulphide at 270°, benzoic acid and a compound melting at 241° are formed. Cēnanthaldehyde and ammonium sulphide when heated at 300° yield cēnanthylamide, melting at 95°; benzaldehyde reacts much more readily, and yields more benzoic acid than benzamide. N. H. M.

Perkin's Reaction. By H. W. SALOMONSON (*Rec. Trav. Chim.*, 6, 23—30).—Benzaldehyde, ethyl succinate, and acetic anhydride were heated together at 125°, 140°, 180°, and 200° for six hours, but no reaction took place. Nitrobenzaldehyde and sodium succinate were heated together under various conditions but without the presence of acetic anhydride; no reaction took place. Meta- or para-nitrobenzaldehyde heated at 180—200° with sodium succinate and glacial acetic acid yields a small quantity of nitrocinnamic acid, but no nitrophenylparaconic acid.

It follows that ethyl succinate cannot be substituted for sodium succinate, or acetic acid for acetic anhydride, and it would seem that the reaction depends on the simultaneous presence of a sodium salt and an anhydride. Perkin showed that even at 100° sodium succinate is decomposed by acetic anhydride, with formation of sodium acetate and succinic anhydride, but the author finds that this reaction takes place only to a very limited extent, and there is little doubt that a condition of equilibrium is established between sodium succinate, acetic anhydride, sodium acetate and succinic anhydride. When one of these substances is removed by the action of the aldehyde, a further quantity of the same substance is formed, which is again removed by the aldehyde, and so on.

The assumption that the action takes place between the sodium salt and the aldehyde will not explain why acetic acid cannot be substituted for acetic anhydride, or ethyl succinate for sodium succinate, but these facts are explained at once, if it is assumed that the action takes place between the aldehyde and succinic anhydride. The acetic anhydride liberates a small quantity of succinic anhydride from the sodium salt with formation of sodium acetate, and as fast as the

succinic anhydride reacts with the aldehyde, a fresh quantity is liberated in the nascent state until decomposition is complete. The advantage gained by using acetic anhydride in place of the anhydride corresponding with the sodium salt is due to the fact that in the latter case the anhydride is in the free state from the beginning, and is not liberated in the nascent condition during the reaction. Acetic anhydride and ethyl succinate do not interact, and the avidity of the aldehyde for the ethyl succinate is not sufficient to produce direct action.

Sodium propionate and the sodium salts of bibasic acids of the paraffin series react directly with benzaldehyde.

Perkin's reaction is strictly analogous to the aldol reaction of Wurtz. C. H. B.

Phenylsalicylic Acid and Diphenyleneketone Oxide. By C. GRAEBE (*Ber.*, **21**, 501—504).—*Phenylsalicylic acid*, $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, is prepared by adding the calculated amount of sodium in small pieces to phenyl salicylate, heated at $280\text{--}300^\circ$: when cold, the product is treated with alcohol, extracted with water, filtered, and precipitated with hydrochloric acid. The precipitate is redissolved in sodium carbonate, precipitated and crystallised from dilute alcohol, from which it separates in plates melting at 113° . It is readily soluble in alcohol and ether, and distils at 355° with slight decomposition into diphenylene- α -ketone oxide. The *silver salt* is sparingly soluble. The *methyl salt* is insoluble in alkalis. When the acid is heated with 10 parts of sulphuric acid, it is converted almost quantitatively into diphenyleneketone oxide; the constitution of the latter compound is therefore $\text{C}_6\text{H}_4\text{--}\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}\text{--C}_6\text{H}_4$. N. H. M.

Paramethoxyphenylacrylic Acid. By A. EINHORN and J. P. GRABFIELD (*Annalen*, **243**, 362—378).—*Paramethoxyphenylacryl methyl ketone*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{COMe}$, is prepared by agitating a mixture of anisaldehyde, acetone, and a solution of sodium hydroxide. The compound melts at 73° , and dissolves freely in ether, alcohol, benzene, and acetic acid. It is converted into paramethoxyphenylacrylic acid (described by Perkin, this Journal, 1877, i, 408) by treatment with sodium hypochlorite. When the methyl ketone is poured into a mixture of sulphuric and nitric acids at 0° , a *nitro-derivative*, $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CH}:\text{CH}\cdot\text{COMe}$, and other products are formed; this is soluble in water, alcohol, ether, ethyl acetate, and benzene, yields metanitroanisic acid on oxidation with potassium permanganate, and can also be prepared by agitating a mixture of metanitroparamethoxybenzaldehyde and acetone with an aqueous solution of sodium hydroxide.

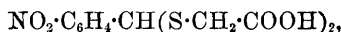
By the nitration of paramethoxyphenylacrylic acid, metanitroparamethoxyphenylacrylic acid and *metunitroparamethoxyphenylethylene* are formed. The latter, $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CH}:\text{CH}_2$, forms rhombic crystals and melts at 89° . It is volatile in a current of steam, and is soluble in the ordinary solvents. It unites directly with two atoms of bromine forming a crystalline dibromide melting at $78\text{--}79^\circ$.

Dinitroparamethoxyphenylethylene can be separated from the mono-nitro-product by its insolubility in chloroform. The dinitro-compound melts at $162-163^{\circ}$, and is deposited from alcohol in needles. It forms an additive compound with bromine. *Metanitroparamethoxybenzaldehyde* crystallises in yellow prisms, and melts at 83.5° . It is soluble in the usual solvents, and forms a compound with phenylhydrazine, melting at 130.5° . It is converted by Perkin's reaction into *metanitroparamethoxycinnamic acid*. This melts at 140° , and dissolves in ether, hot water, and alcohol. The methyl salt melts at 125° . Nitromethoxycinnamic acid does not form an additive compound with hydrobromic acid, but by the action of an ethereal solution of hydrogen bromide on the acid at 90° , ethyl bromide and ethyl nitromethoxyphenylacrylate are produced. The ethyl salt melts at 100° . At 100° , an acetic acid solution of hydrogen bromide converts nitromethoxyphenylacrylic acid into *metanitroparahydroxyphenylacrylic acid*; this crystallises in needles, melts at 198° , does not unite with hydrogen bromide, but unites with bromine (in ethereal solution) to form a dibromide. Nitromethoxycinnamic acid readily absorbs bromine forming *metanitroparamethoxyphenyldibromopropionic acid*, $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{COOH}$, which melts at 178° , and is decomposed by a cold solution of potassium hydroxide, losing 1 mol. HBr and yielding nitromethoxyphenylbromacrylic acid. Alcoholic potassium hydroxide removes 2 mols. HBr, and converts the dibromide into *metanitroparamethoxyphenylpropionic acid*. W. C. W.

Compounds of Aldehydes, Ketones, and Ketonic Acids with Thioglycollic Acid. By J. BONGARTZ (*Ber.*, 21, 478-487).—*Ethylidenedithioglycollic acid*, $\text{CHMe}(\text{S}\cdot\text{CH}_2\cdot\text{COOH})_2$, is formed when acetaldehyde is mixed with thioglycollic acid; the product when kept in a vacuum crystallises to a white mass, which can be recrystallised from chloroform. It melts at $107-108^{\circ}$.

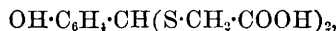
Benzylidenedithioglycollic acid, $\text{CHPh}(\text{S}\cdot\text{CH}_2\cdot\text{COOH})_2$, crystallises from hot water (20 to 30 parts) in well-formed needles, melting at $123-124^{\circ}$.

Orthonitrobenzylidenedithioglycollic acid,



crystallises from hot chloroform in colourless crystals which gradually become yellow when exposed to light, and melt at $122-123^{\circ}$. The *meta*-compound crystallises from 10 per cent. acetic acid in needles, melting at $129-130^{\circ}$. The *para*-derivative crystallises from dilute acetic acid in lustrous, yellowish needles, melting at $161-162^{\circ}$.

Orthohydroxybenzylidenedithioglycollic acid,



is prepared by treating a mixture of salicylaldehyde and thioglycollic acid with zinc chloride; it is readily soluble in hot water, alcohol, and ether, insoluble in benzene, light petroleum, and chloroform, and melts at $147-148^{\circ}$.

Cinnamaldehydedithioglycollic acid, $\text{CHPh}:\text{CH}\cdot\text{CH}(\text{S}\cdot\text{CH}_2\cdot\text{COOH})_2$, crystallises from hot water in white plates, melting at $142-143^{\circ}$,

and when reduced with zinc-dust in alkaline solution yields the *compound* $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{COOH}$; this crystallises in plates of a silky lustre, melting at $76-77^\circ$.

Furfuraldehydedithioglycollic acid, $\text{C}_4\text{H}_3\text{O}\cdot\text{CH}(\text{S}\cdot\text{CH}_2\cdot\text{COOH})_2$, melts at $104-105^\circ$ with decomposition; it could not be obtained quite pure.

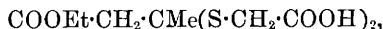
Dimethylmethylenedithioglycollic acid, $\text{CMe}_2(\text{S}\cdot\text{CH}_2\cdot\text{COOH})_2$, separates from chloroform in clear crystals, melting at $126-127^\circ$.

Methylphenylmethylenedithioglycollic acid, $\text{CMePh}(\text{S}\cdot\text{CH}_2\cdot\text{COOH})_2$, crystallises from water in colourless needles, melting at $135-136^\circ$.

Diphenylmethylenedithioglycollic acid, $\text{CPh}_2(\text{S}\cdot\text{CH}_2\cdot\text{COOH})_2$, is obtained by heating benzophenone and thioglycollic acid with zinc chloride for several hours, and crystallises from hot dilute acetic acid in colourless needles, which melt at $175-176^\circ$ with evolution of carbonic anhydride.

The additive compounds of pyruvic and thioglycollic acids have already been described (Abstr., 1886, 938).

Ethyl acetoacetate dithioglycollic acid,



is prepared by passing dry hydrogen chloride through a mixture of ethyl acetoacetate and thioglycollic acid; it forms a white, crystalline powder, readily soluble in warm water and cold alcohol, almost insoluble in light petroleum, and melts at $95-96^\circ$.

Levulodithioglycollic acid,



crystallises from water in needles melting at $153-154^\circ$, and is very stable towards alkalis.

When a dilute aqueous solution of benzyldenedithioglycollic acid (2 grams) is shaken with a solution of 4 grams of potassium permanganate in 1 litre of water, the *disulphone*, $\text{CHPh}(\text{SO}_2\text{Me})_2$, is formed. This crystallises in slender needles, melting at $162-163^\circ$, readily soluble in hot water, sparingly soluble in ether. The same compound is also formed by the oxidation of *dithiomethylbenzylidene*, $\text{CHPh}(\text{SMe})_2$. This is prepared by the action of gaseous hydrogen chloride on a mixture of benzaldehyde and methyl mercaptan, and forms a colourless, mobile liquid.

The disulphones of meta- and para-nitrobenzylidene prepared from the corresponding acids both crystallise in slender, yellowish needles, which melt at $178-179^\circ$ and at $247-248^\circ$ respectively.

N. H. M.

Preparation and Nitration of Dibenzylmalonic Acid. By J. C. A. S. THOMAS (*Rec. Trav. Chim.*, 6, 87-90).—Ethyl dibenzylmalonate obtained by the interaction of ethyl malonate, alcohol, sodium, and benzyl chloride, forms white crystals melting at $13-14^\circ$. 30 grams of this ethereal salt is dissolved in 20-30 c.c. of alcohol, and 20 grams of potash added gradually in coarse powder. Heat is developed, but on cooling the mass becomes almost solid. It is allowed to stand overnight, and is heated to drive off the alcohol. The product then separates into two layers, the upper consisting probably of half-saponified salt. Concentrated aqueous potash is added,

and the mixture heated on a water-bath for several hours and then acidified with hydrochloric acid. Evolution of carbonic anhydride indicates the formation of some dibenzylacetic acid. Dibenzylmalonic and dibenzylacetic acids are separated by taking advantage of the fact that the former is somewhat soluble in water, but is insoluble in light petroleum; whilst the latter is almost insoluble in boiling water, but is somewhat soluble in light petroleum. Dibenzylmalonic acid crystallises in needles, which melt at 171° , as stated by Perkin (*Trans.*, 1885, 821), and when added to cooled nitric acid of sp. gr. 1.52, precipitated with water, and the product purified by solution in acetic acid and precipitation with water, it yields a dinitro-derivative, $C_{17}H_{14}N_2O_8$; this forms a white crystalline powder, melting at 155° , with evolution of gas. This product is not homogeneous, for if the acetic acid solution is fractionally precipitated by adding water, the first fraction melts at 160° , and the last becomes soft at 95° , and is completely melted at 110° . C. H. B.

Nitrophenylparaconic Acids. By H. W. SALOMONSON (*Rec. Trav. Chim.*, 6, 1—22).—Phenylparaconic acid can be converted into α -naphthol with intermediate formation of phenylisocrotonic acid, and the author prepared the nitrophenylparaconic acid with a view to obtain nitronaphthol in a similar manner. Nitrophenylparaconic acid, however, does not yield nitrophenylisocrotonic acid, and hence does not yield nitronaphthol.

Metanitrobenzaldehyde, sodium succinate, and acetic anhydride, in molecular proportion, were heated together at 125° for four hours, the product treated with water, the solution extracted with ether, and the aqueous liquid acidified with hydrochloric acid. A precipitate is thus obtained which can readily be crystallised from warm water. The ethereal solution, which contains metanitrobenzoic acid and metanitrophenylparaconic acid, is neutralised with sodium carbonate, acidified with hydrochloric acid, and the precipitate subjected to fractional crystallisation. The metanitrobenzoic acid melts at 141° .

Metanitrophenylparaconic acid melts at 171° . Neither the acid nor its salts contain water of crystallisation, and in this respect it differs from phenylparaconic acid. The acid cannot be distilled in a vacuum, and carbonises at 230 — 250° , these properties being common to all its derivatives. It is carbonised when heated with water in sealed tubes at 200 — 220° , but is not decomposed by dilute sulphuric acid under the ordinary pressure, and is not affected by dilute sulphuric acid, glacial acetic acid, or acetic anhydride, in sealed tubes at 170° , although at a higher temperature it carbonises. It is dissolved by cold concentrated sulphuric acid, and is precipitated unchanged on addition of water, even if the solution has been heated to the point of carbonisation. Metanitrophenylparaconic acid is soluble in warm water, alcohol, glacial acetic acid, ethyl acetate, and glycerol, but not in carbon bisulphide or benzene.

Since metanitrophenylparaconic acid is the lactone of nitrophenylitamalic acid, it forms two series of salts. *Barium metanitrophenylitamalate*, $NO_2 \cdot C_6H_4 \cdot CH(OH) \cdot CH < \begin{smallmatrix} CH_2 \cdot COO \\ -COO- \end{smallmatrix} > Ba$, is obtained by

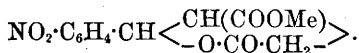
dissolving the acid in ammonia, adding a solution of barium chloride, and boiling for a short time. The metanitrophenylparaconates are obtained by dissolving the acid in ammonia, heating to expel excess of ammonia, and adding soluble metallic salts. The silver salt forms colourless needles; the copper salt pale blue crystals; and the lead salt small needles.

Paranitrophenylparaconic acid is obtained from paranitrobenzaldehyde in a precisely similar manner. It crystallises from boiling water in small, white, nacreous leaflets; from acetic acid in cubes. It melts at 163° , and is soluble in warm water, ethyl acetate, alcohol, and sulphuric acid; is slightly soluble in ether, but does not dissolve in cold water, light petroleum, benzene, or carbon bisulphide. With barium hydroxide, it yields *barium paranitrophenylitamalate*, which forms small white crystals. *Silver paranitrophenylparaconate* crystallises in needles; the copper salt also crystallises from water.

Both the meta- and para-derivatives are strong acids, and liberate acetic acid from sodium acetate.

Barium paranitrophenylitamalate, when treated with hydrochloric acid in the cold, the solution extracted with ether, and the ethereal solution allowed to evaporate spontaneously, yields free paranitrophenylitamalic acid as a yellow amorphous residue. If a solution of nitrophenylparaconic acid in concentrated ammonia is heated with acetic acid, and then mixed with barium chloride, no precipitate is formed, hence it is evident that nitrophenylitamalic acid is converted by acetic acid into nitrophenylparaconic acid.

If a solution of meta- or para-nitrophenylparaconic acid in methyl alcohol is saturated with hydrogen chloride, and then mixed with water, it yields a resinous precipitate, which, after being dried for a week over potassium hydroxide and sulphuric acid, contains no chlorine, from which it follows that the lactone-group has remained intact. The resinous product is the methyl salt of the acid



Ethyl paranitrophenylparaconate is obtained by heating the acid and alcohol with strong sulphuric acid. Its properties are similar to those of the methyl salt. Both are soluble in benzene, ether, sulphuric acid, and chloroform.

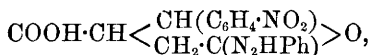
Both acids are rapidly reduced by tin and hydrochloric acid at the ordinary temperature, but the products can only be isolated in the form of platinumchlorides, which are easily soluble in water and alcohol, but are insoluble in benzene, ether, and chloroform. The product of reduction is amidophenylparaconic acid, and the platinum salt has the composition $(\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} < \begin{array}{c} \text{CH}(\text{COOH}) \\ -\text{O} \cdot \text{CO} \cdot \text{CH}_2- \end{array} >)_2, \text{H}_2\text{PtCl}_6$.

The hydrochloric acid solution of the amido-acid gives no precipitate with gold chloride, or sulphuric, hydrobromic, hydriodic, or acetic acids. If after reduction and separation of the tin the solution is rapidly concentrated until viscous, and placed in a vacuum over potash and sulphuric acid, the metamidophenylparaconic acid will sometimes crystallise, but the para-derivative always remains as a

syrup. If the liquid is now heated to 60–70° to expel water and hydrogen chloride, the amido-acid is obtained in groups of prismatic crystals, insoluble in benzene, chloroform, and ether, but very hygroscopic, and easily soluble in water or ethyl alcohol. If heated rapidly it carbonises; with nitrous acid, no diazo-compound is obtained.

Hydriodic acid completely reduces both the nitro-acids when heated in sealed tubes at 130°, but not at 100°. This method, however, is inconvenient.

Metanitrophenylparaconic acid, heated at 130° with phenylhydrazine in molecular proportion, allowed to cool, and treated first with dilute acetic acid and then with warm water, yields a derivative,



which melts at 130–132° with decomposition.

Orthonitrophenylparaconic acid was obtained in a similar manner, but the yield was small, and the acid was not isolated. C. H. B.

Formation of Monosulphones. By R. OTTO (*Ber.*, 21, 652–658).—When methylene-iodophenylsulphone reacts with sodium benzenesulphinate in alkaline solution, in sealed tubes at about 200°, the products are methylphenylsulphone, ethyl ether, phenyl mercaptan, ethylphenyl sulphide, phenyl bisulphide, iodine, hydriodic acid, benzenesulphonic acid, and sodium iodide, benzenesulphonate, sulphate, and iodate. The primary reaction is evidently that in which the methylphenylsulphone is formed; most of the other products being due to secondary reactions. The reaction between methylene-iodoparatolylsulphone and sodium paratoluenesulphinate seems to be quite analogous, methylparatolylsulphone being formed.

Methylene-iodoparatolylsulphone is prepared by heating equimolecular proportions of sodium toluenesulphinate and methylene iodide dissolved in alcohol, in a reflux apparatus; it forms small needles, and melts at 136°.

When methylene-iodophenylsulphone is heated with sodium ethoxide and alcohol at 70–80°, it is readily converted into methylphenylsulphone; in this case, the eliminated oxygen is mainly used up in converting the iodide into iodate; although small quantities of other oxidation products are formed. In the case of the corresponding chloro-compound, benzenesulphinic acid is also formed.

By the action of sodium ethoxide on dichloromethylphenylsulphone in alcoholic solution, the latter is converted partly into the monochloro-derivative, partly into sodium benzenesulphonate with a trace of sulphinate.

From these and other experiments, some of which are not yet published, the author deduces the law:—Dihalogen-derivatives of hydrocarbons, fatty acids, and their ethereal salts, in which the halogen-atoms are united to the same carbon-atom, when treated with alkaline sulphinates only exchange a single halogen-atom for the group $\text{R}'\text{SO}_2$; the second halogen-atom, in the presence of water, being displaced by hydrogen.

A. J. G.

Methylenechlorophenylsulphone. By R. OTTO (*Ber.*, **21**, 658—659).—*Methylenechlorophenylsulphone*, $\text{CH}_2\text{Cl}\cdot\text{SO}_2\text{Ph}$, is best prepared by heating an aqueous solution of sodium dichloracetate and sodium benzenesulphinat in molecular proportions. It crystallises in plates, melts at 52° , and is readily soluble in hot alcohol, nearly insoluble in cold water. It is not formed by the action of chlorine on a solution of methylphenylsulphone in carbon tetrachloride. When reduced with sodium amalgam in alcoholic solution, it yields sodium benzenesulphinat and some gaseous product, probably ethane or ethylene. With zinc and sulphuric acid, it gives methylphenylsulphone.

Attempts to convert it into ethylenediphenylsulphone by the action of sodium or sodium-amalgam in benzene solution, were without result.

A. J. G.

Identity of Diphenyldiisindole and 3' Phenylindole. By R. MÖHLAU (*Ber.*, **21**, 510—511).—A comparison of diphenyldiisindole and 3' phenylindole showed them to be identical, and a vapour-density determination made with the former compound pointed to the formula $\text{C}_{14}\text{H}_{11}\text{N}$, and not $\text{C}_{28}\text{H}_{22}\text{N}_2$ (*Abstr.*, 1883, 342. Compare also Wolff, this vol., p. 371.)

N. H. M.

Indolecarboxylic Acids. By G. CIAMICIAN and G. MAGNANINI (*Ber.*, **21**, 671—673).—Carboxylic acids cannot be prepared from methylketole and scatole by the ammonium carbonate reaction, but are readily obtained by heating with sodium in a stream of carbonic anhydride at $230\text{--}250^\circ$.

Methylketolecarboxylic acid crystallises in needles, and decomposes into methylketole and carbonic anhydride when heated alone at 183° , or when its ammoniacal solution is heated. The scatolecarboxylic acid is identical with that described by H. and E. Salkowski (*Abstr.*, 1880, 413; 1885, 569).

When acetylmethylketole is oxidised with potassium permanganate, it yields acetylorthamidobenzoic acid; when, however, the oxidation is effected by fusion with potash, α -indolecarboxylic acid is formed. The same acid is obtained when methylketole is fused with potash, whilst scatole yields β -indolecarboxylic acid.

Acetylscatole is best prepared by the action of acetic chloride and some zinc chloride on scatole at the ordinary temperature; it forms long, slender needles, and melts at $147\text{--}148^\circ$.

A. J. G.

Hydrogenation of Triphenylmethane. By M. GOLENKIN (*J. Russ. Chem. Soc.*, 1887, 166—171).—For the purpose of hydrogenation, 1 gram of triphenylmethane was sealed up in tubes with 15 c.c. of hydriodic acid and 0.5 gram of red phosphorus, and the mixture heated gradually to 280° , the tubes being opened and sealed up again several times in order to remove the gases formed in large quantities. When the reaction was over, the tubes were found to contain a small quantity of liquid hydrocarbon (3.5 grams from 12 grams of triphenylmethane) consisting of a mixture of benzene and toluene, but no hydrogenation of the triphenylmethane took place.

B. B.

Derivatives of Orthotolidine. By A. GERBER (*Ber.*, **21**, 746—750).—*Diacetylorthotolidine*, $C_{14}H_{12}(NHAc)_2$, obtained by heating tolidine with glacial acetic acid in a reflux apparatus, forms lustrous, white needles, melts at 314° , sublimes at a still higher temperature with partial decomposition, and only dissolves readily in phenol.

Tetracetylorthotolidine, $C_{14}H_{12}(NAc)_4$, is prepared by heating the diacetyl compound with acetic anhydride at 160 — 170° for about six hours; it forms snow-white, lustrous needles, melts at 211° , and is very readily soluble in the ordinary solvents. When heated with concentrated hydrochloric acid, it is reconverted into the diacetyl compound.

Dinitrodiacetylorthotolidide, $C_{14}H_{12}(NHAc)_2(NO_2)_2$, forms nearly white crystals, decomposes without previous fusion at 320° . When saponified, it yields *dinitro-orthotolidine* [$Me_2 : (NH_2)_2 : (NO_2)_2 = 3 : 3' : 4 : 4' : 5 : 5'$]; this forms shimmering, garnet-red needles, melts at 266 — 267° , explodes at a few degrees higher, and when reduced with zinc-dust, is converted into a ditoluylenediamine which yields an azine with phenanthraquinone, and therefore must have the amido-groups in the ortho-position.

Orthodicresol, $C_{14}H_{12}(OH)_2$, is prepared by diazotising orthotolidine and boiling the product with dilute sulphuric acid. It forms a white, crystalline powder, melts at 160 — 161° , and is sparingly soluble in boiling water, readily in alcohol, ether, acetic acid, and in boiling benzene hydrocarbons. A *dinitro*-derivative is prepared by boiling the diazotised product with nitric acid; it crystallises in golden-yellow needles, melts at 272 — 273° , sublimes with partial decomposition, is insoluble in water, alcohol, and ether, and dissolves in hot alkalis to form salts which crystallise in stellate groups; the potassium and sodium salts are reddish-violet, the ammonium salt orange-red.

A. J. G.

Thio-derivatives of Desoxybenzoïn and its Analogues. By V. MEYER (*Ber.*, **21**, 353—355).—The compound obtained by Bergreen by the action of thiocarbonyl chloride on sodium ethoxide and desoxybenzoïn (this vol., p. 446) possesses much interest, since, in addition to its remarkable properties, it affords the first instance of the displacement of both hydrogen-atoms of the methylene group in desoxybenzoïn by a radicle containing carbon (compare this vol., p. 147). The compound has a fiery, golden-yellow colour, and in appearance resembles the most beautiful yellow organic dyes. Concentrated sulphuric acid dissolves it, forming a deep violet-coloured solution from which water precipitates the compound unchanged. When heated with pyrosulphuric acid, it is converted into a yellow sulphonic acid, which yields a sparingly soluble barium salt and readily soluble alkaline salts. The substance itself, however, is too sparingly soluble to admit of its employment as a dye, whilst the sulphonic acid is almost destitute of tinctorial properties. It is improbable that the compound has the composition expressed by the formula $CO \cdot Ph \cdot CPh \cdot CS$, since this would in no way correspond with its properties, which differ in so marked a manner from those of the thio-derivatives of ethyl malonate and ethyl acetoacetate prepared under like conditions by Bergreen (*loc. cit.*); on the contrary, the author

regards it as a polymeride, and proposes to determine its molecular weight by Raoult's method: in the meantime, it is suggested that it is either a derivative of a six-carbon "ring" or a thiophen-derivative formed by a condensation analogous to that occurring in the formation of thiazoles (this vol., p. 256).

The ketones, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$ and $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{SH}_3$, form corresponding compounds when treated with thiocarbonyl chloride and, under like conditions, the phenylated desoxybenzoin,



also yields a yellow compound which, however, dissolves in sulphuric acid with a green colour. These compounds are extremely stable; the thiophen-derivative for example, when heated with fuming nitric acid is converted into a yellow nitro-derivative, which gives no colour reaction with sulphuric acid.

Methyl-desoxybenzoin, $\text{COPh}\cdot\text{CHMePh}$, and its homologues do not react with thiocarbonyl chloride, and hence this reagent affords a ready means of discriminating between primary and secondary derivatives of desoxybenzoin.

Thiocarbonyl chloride cannot be employed to distinguish between primary and secondary benzyl cyanides. Benzyl cyanide, however, reacts with a mixture of sodium ethoxide (1.4 parts of sodium in 20 parts of alcohol) and benzaldehyde forming the nitrile of phenyl-cinnamic acid, $\text{CHPh}\cdot\text{CPh}\cdot\text{CN}$, which melts at 88° , whilst the nitrile of hydratropic acid, $\text{CHMePh}\cdot\text{CN}$, does not form a condensation compound under similar conditions. This method can not only be used qualitatively, but may also be employed to separate benzyl cyanide from a mixture of the two compounds.

W. P. W.

Oximes of Benzil. By N. POLONOWSKA (*Ber.*, **21**, 488—491).—When benzilmonoxime in alcoholic solution is reduced with $2\frac{1}{2}$ per cent. sodium amalgam in presence of acetic acid, diphenylhydroxyethylamine is obtained. No tetraphenylaldine is formed, as when the reduction is effected by means of tin and hydrochloric acid (Braun and Meyer, this vol., p. 367). When benzildioxime is reduced with sodium amalgam, tetraphenylaldine (*loc. cit.*) is obtained; ammonia is formed in the reaction. The yield of tetraphenylaldine is small.

N. H. M.

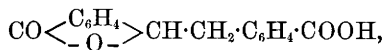
Intramolecular Change in Benzildioxime. By E. GÜNTHER (*Ber.*, **21**, 516—518).—When benzildioxime is heated with a solution of hydrogen chloride in glacial acetic acid and acetic anhydride, a diacetyl-compound is formed which, when saponified, yields Goldschmidt's isobenzildioxime, melting at 206° (*Abstr.*, 1884, 62).

The compound (m. p. 121 — 122°) obtained by the action of phosphorus pentachloride on benzildioxime (Beckmann, *Abstr.*, 1837, 826) is a dichloride, $\text{NCl}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{NCl}$; two other nitrogenous compounds melting at 146° and 95° respectively, are also formed in the reaction. The chloride could not be obtained from isobenzildioxime.

N. H. M.

Hydrodiphthallactonic Acid and Hydrodiphthalyl. By E. HASSELBACH (*Annalen*, **243**, 249—272).—Wislicenus (*Abstr.*, 1885, VOL. I. IV. 2 k

57) has shown that diphthalyl, hydrodiphthalyl, and hydrodiphthallactonic acid are formed by the action of acetic acid and zinc-dust on phthalic anhydride, also that hydrodiphthallactonic acid,

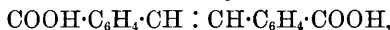


is converted into hydroxydiphthalyllic acid,



by boiling with potash.

Silver hydroxydiphthalylate decomposes at 225° in a vacuum, yielding water, phthalic anhydride, and other products. The *ethyl* salt is a thick liquid which slowly crystallises. Hydrodiphthallactonic acid is converted into *stilbenediorthocarboxylic acid*,



by the action of potassium cyanide at 215°. This acid when reduced with hydriodic acid forms dibenzyl diorthocarboxylic acid. Stilbene diorthocarboxylic acid begins to melt at 250°, and is converted at this temperature into hydrodiphthallactonic acid. The ethyl salt forms small needles and melts at 79–80°.

Hydrodiphthalyl (m. p. 250°) dissolves in alkalis, yielding salts of dihydroxybenzyl diorthocarboxylic acid, $\text{C}_{16}\text{H}_{14}\text{O}_6$. The free acid has not been isolated; on the addition of acetic acid to its salts, an acid is deposited having the composition $\text{C}_{16}\text{H}_{12}\text{O}_5$; this acid is converted into hydrodiphthalyl at 190° or by heating with acetic anhydride. The precipitate which is formed when hydrochloric acid is added to a solution of hydrodiphthalyl in alkalis is not a definite chemical compound, but a mixture consisting chiefly of hydrodiphthalyl. Hydrodiphthallactonic acid is not the sole product of the reduction of diphthalyl with zinc and potassium hydroxide; hydrodiphthalyl is always formed in small quantities. Hydrodiphthalyl is partly converted into hydrodiphthallactonic acid by reduction with zinc-dust in alkaline solutions.

W. C. W.

Derivatives of α -Naphthol. By O. N. WITT (*Ber.*, 21, 321–325).—In addition to α -naphtholsulphonic acid, *α -hydroxynaphthyl methyl ketone*, $\text{OH} \cdot \text{C}_{10}\text{H}_7 \cdot \text{COMe}$, is obtained on sulphonating α -naphthol in acetic acid solution, and is also formed by heating equal weights of α -naphthol and acetic acid with zinc chloride as in Nencki and Sieber's method of preparing analogous compounds (*Abstr.*, 1881, 591, 811). It crystallises from benzene in six-sided prisms, from alcohol in needles, melts at 103°, has a pale-green colour, and is insoluble in water. Sulphuric acid dissolves it with a red, alkalis with a pure yellow colour. The alkaline salts crystallise in long, citron-yellow needles, and are decomposed by carbonic anhydride. In alkaline solution, it yields an intense reddish-brown colour with orthonitrobenzaldehyde, but does not form an indophenol on treatment with paradiamines either in the presence of air or of oxidising agents. A comparison of the azo-colours obtained from the ketone with the corresponding α -naphthol-derivatives shows that the shade of colour is invariably more yellow in the case of the former. The *crime*

crystallises from dilute alcohol in long, pale-yellow needles, and melts at 168—170° with decomposition. When heated with 12 per cent. alcoholic ammonia at 180—200°, the ketone is converted into the *ketimide*, $\text{OH}\cdot\text{C}_{10}\text{H}_7\cdot\text{CMe}\cdot\text{NH}$, which crystallises from alcohol in long, golden-yellow needles, melts at 203° with decomposition, and is decomposed into its constituents on treatment with acids or alkalis.

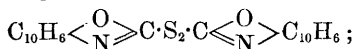
β -Naphthol, when heated with acetic acid and zinc chloride, does not form a compound corresponding with α -hydroxynaphthyl methyl ketone.

W. P. W.

Action of Carbon Bisulphide on Benzene-azo- β -Naphthol.

By P. JACOBSON (*Ber.*, 21, 414—422).—By the action of carbon bisulphide on benzene-azo- β -naphthol, phenyl thiocarbimide, sulphur, thiocarbamidonaphthol, and carbanilamidonaphthol are formed. This reaction shows that under certain conditions benzene-azo- β -naphthol is capable of reacting as though it were a true azo-compound, for its explanation is difficult on the hydrazide formulæ proposed by Liebermann (*Abstr.*, 1884, 610) and by Zincke and Lawson (*Ber.*, 20, 2903), although at the same time the insolubility in alkalis precludes the substance being regarded as an azo-compound.

Thiocarbamidonaphthol, $\text{C}_{10}\text{H}_7\langle\text{N}\rangle\text{C}\cdot\text{SH}$, is obtained, together with the products mentioned above, by heating benzene-azo- β -naphthol with five times its weight of carbon bisulphide for 8 to 12 hours at 250°; it is separated from the other products by means of its insolubility in carbon bisulphide and its solubility in alkalis. It crystallises in long, colourless needles, melts at 248—249°, and is sparingly soluble in benzene, readily soluble in hot acetic acid, and very readily soluble in cold alcohol. When heated for some hours at 150—180° with hydrochloric acid, it yields amido- β -naphthol. From the latter, it can be re-formed by heating with carbon bisulphide. When boiled with aniline, hydrogen sulphide is evolved and carbanilamidonaphthol formed. By the action of an alcoholic solution of iodine, it is converted into the corresponding *bisulphide*,



this crystallises in tufts of microscopic needles, is readily soluble in hot benzene and acetic acid, nearly insoluble in hot alcohol.

Carbanilamidonaphthol, $\text{C}_{10}\text{H}_7\langle\text{N}\rangle\text{C}\cdot\text{NHPh}$, the main product of the reaction, forms small colourless needles, melts at 167—168°, and is very readily soluble in cold alcohol, sparingly soluble in boiling hydrochloric acid, and insoluble in alkalis. The *acetate* crystallises in lustrous, flat needles and melts at 120—130°. The *picrate* melts at 209—210°. When heated with hydrochloric acid for four hours at 180—190°, it is resolved into amidonaphthol, carbonic anhydride, and aniline.

A. J. G.

Substitution of the Acetyl-group for the Amido-group by Aid of the Diazo-reaction. By R. MELDOLA (*Ber.*, 21, 601).—The compounds formed by the action of nitrous acid on *meta*- and *para*-

nitrobenzene-azo- β -naphthylamine are readily decomposed by glacial acetic acid with formation of the acetyl-derivatives of the corresponding β -naphthol-compounds. For instance, if nitrobenzene-azo- β -naphthylamine is dissolved in hot (not boiling) acetic acid and the necessary amount of sodium nitrite added, *metanitrobenzene-azoacetyl- β -naphthol* soon separates; it crystallises in hair-like, red needles, and melts at $161-162^\circ$; when heated for $\frac{1}{2}$ hour with alcoholic potash, *metanitrobenzene-azo- β -naphthol* is readily obtained.

This method gives a means of displacing the amido-group by the acetyl-group, and will probably be of general applicability for the synthesis of phenol-derivatives containing different acid radicles.

A. J. G.

Nitro-derivatives of Phenyl- β -Naphthylamine. By E. HEIM (*Ber.*, **21**, 589—594).—*Dinitrophenyl- β -naphthylamine*,



is formed by the action of bromodinitrobenzene (m. p. 72°) on an alcoholic solution of β -naphthylamine. It crystallises in crimson prisms, melts at 169.5° , is soluble in acetic acid, acetone, hot benzene, and ether, very sparingly soluble in alcohol, and insoluble in water. The reduction-products obtained by the action of iron and acetic acid, and of stannous chloride and hydrochloric acid, could not be isolated.

Nitramidophenyl- β -naphthylamine, $[\text{NH} : \text{NH}_2 : \text{NO}_2 = 1 : 2 : 4]$, is prepared by reducing the dinitro-compound with ammonium sulphide; it is dimorphous, crystallising in brown needles of cantharidine lustre, or in small, crimson prisms, it melts at 195° ; and is very readily soluble in ether, acetic acid, acetone, and chloroform, moderately soluble in alcohol, benzene, and its homologues, insoluble in light petroleum. The acetyl-derivative forms lustrous, orange-red needles, which melt below 200° with decomposition.

Nitrophenylethenylamido- β -naphthylamine, $\text{C}_{10}\text{H}_7\cdot\text{N} < \begin{smallmatrix} \text{C}_6\text{H}_3(\text{NO}_2) \\ \text{CMe}=\text{N} \end{smallmatrix} >$, is prepared by heating nitramidophenyl- β -naphthylamine with ten times its weight of acetic anhydride for seven hours in a reflux apparatus; it forms pale-yellow, lustrous needles, melts at 162° , is readily soluble in alcohol and ether, still more so in benzene, toluene, acetone, and chloroform, and dissolves in acids. The formation of this anhydro-base leaves no doubt that in nitramidophenyl- β -naphthylamine, the amido- and imido-groups are relatively in the ortho-position.

Nitrazoimidophenyl- β -naphthylamine, $\text{C}_{10}\text{H}_7\cdot\text{N} < \begin{smallmatrix} \text{C}_6\text{H}_3(\text{NO}_2) \\ \text{N}=\text{N} \end{smallmatrix} >$, is obtained by the action of nitrous acid on the nitramido-compound; it crystallises in delicate, white needles, melts at $203-204^\circ$, is sparingly soluble in alcohol, readily in ether, acetic acid, benzene, chloroform, and acetone, and is indifferent to reagents.

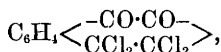
A. J. G.

Ketonaphthol (Aceto- α -Naphthol). By H. ERDMANN (*Ber.*, **21**, 635—636).—*Ketonaphthol*, $\text{C}_{10}\text{H}_6\text{Ac}\cdot\text{OH}$ $[\text{OH} : \text{Ac} = 1 : 3]$, was obtained by the author in 1886, by the distillation of benzallevulinic acid; it melts at 167° , is rather sparingly soluble in benzene in the

cold, dissolves in concentrated sulphuric acid with orange-yellow colour, gives intensely yellow compounds with alkalis, unites with diazo-compounds to form colouring matters identical in tint with the corresponding compounds from α -naphthol, and gives indophenol reactions with quinonechlorimides. Witt's α -hydroxynaphthyl methyl ketone (this vol., p. 486) is evidently closely related in properties.

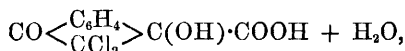
A. J. G.

β -Naphthaquinone. By T. ZINCKE (*Ber.*, **21**, 491—501; compare this vol., p. 158).—*Tetrachlorodiketohydronaphthalene*,



is prepared by passing chlorine into a solution of orthamidonaphthol hydrochloride in 15 parts of glacial acetic acid until the liquid is yellow; the product is kept for two days in a closed vessel, precipitated with water, and crystallised from dilute acetic acid. The anhydrous compound is obtained by heating the substance at 100—105°, and crystallising it from anhydrous ether free from alcohol, some light petroleum being added. It forms large, transparent, lustrous, monoclinic crystals of a pale-sulphur colour, readily soluble in ether, carbon bisulphide, and glacial acetic acid, less soluble in light petroleum; it melts at 90—91°, and decomposes at 180° into dichloro- β -naphthaquinone and chlorine. When the acetic acid solution is heated with potassium iodide, dichloro- β -naphthaquinone is formed. It is converted by stannous chloride and by sulphites into dichloro- β -naphthaquinol. Tetrachlorodiketohydronaphthalene, precipitated by water, forms small, lustrous plates with 3 mols. H_2O , and melts at 86°. It can also be obtained in lustrous needles (with 1 mol. H_2O) which melt at 87°. When the crystals with 3 mols. H_2O are recrystallised from ether, large, monoclinic crystals, melting at 90—91° are obtained, and resemble the anhydrous crystals, except that they are white. When the tetrachloro-compound is crystallised from alcohol, a *monethylate* separates in white crystals, melting with effervescence at 103°.

Dichlorodiketohydroxyhydrindocarboxylic acid,



obtained by dissolving the diketohydrate in dilute sodium carbonate solution, forms large, colourless, monoclinic crystals, melting at 138—139°, readily soluble in alcohol, benzene, and glacial acetic acid, When boiled with baryta-water, it decomposes, probably with formation of the compound $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CCl} \end{smallmatrix} > \text{C} \cdot \text{OH}$. The *methyl salt* forms large, lustrous, monoclinic crystals, melting at 123—124°. The *acetyl-compound*, $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CCl}_2 \end{smallmatrix} > \text{C}(\text{OAc}) \cdot \text{COOH}$, crystallises in small prisms melting at 126°.

Dichloro- α -diketohydrindonaphthene, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{CCl}_2$, prepared by

oxidising the hydroxy-acid with chromic acid, crystallises from dilute alcohol in small, lustrous plates, melting at 124—125°.

Trichlorovinylbenzoylcarboxylic acid, $\text{CCl}_2\text{CCl}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{COOH}$, is formed in small quantity when the tetrachlorodiketone is dissolved in sodium carbonate. It was obtained as an oil, and was not purified.

When the tetrachlorodiketone is dissolved in soda, and the solution acidified with acetic acid and warmed with chromic acid, trichlorovinylbenzoic acid (Abstr., 1887, 955) is obtained.

The diketone, $\text{C}_8\text{H}_4\text{O}_2\text{Cl}_2$, described above, is identical with the compound previously obtained by the action of phosphoric chloride on the hydroxy-derivative from the dichloroketone, $\text{C}_8\text{H}_4\text{OCl}_2$ (Abstr., 1887, 728). The hydroxy-derivative, and the amine by means of which it is obtained, must, therefore, have the constitution represented by the formulæ $\text{CO} < \text{C}_6\text{H}_4 \text{CCl} > \text{C}\cdot\text{OH}$ and $\text{CO} < \text{C}_6\text{H}_4 \text{CCl} > \text{C}\cdot\text{NHR}'$, respectively.

N. H. M.

Action of Bromine on the Naphthaquinoneoximes. By C. BRÖMME (*Ber.*, **21**, 386—391).—When a slight excess of bromine is added to a solution of naphtha- β -quinone- α -oxime in chloroform, an additive compound, $\text{C}_{10}\text{H}_7\text{NO}_2\text{Br}_2$, is formed, which crystallises in colourless needles, melts at 130—131°, and is not very stable. When heated in solution in acetic acid or in alcohol, or when dissolved in alkalis, it loses hydrogen bromide and is converted into *β -bromonaphtha- β -quinone- α -oxime*, $\text{C}_{10}\text{H}_5\text{BrO}\cdot\text{NOH}$ [$\text{NOH} : \text{O} : \text{Br} = 1 : 2 : 3$]; this forms long, yellow needles, melts at 172°, is soluble in alcohol, ether, benzene, chloroform, light petroleum, and acetic acid with brown colour, in concentrated sulphuric acid with purple, and in alkalis with brownish-green colour. It is also formed if the bromination is conducted in acetic acid solution in the cold; if, however, it is effected in hot solution, a *bromonaphthaquinone* is formed which melts at 200—201°, is soluble in alcohol, ether, &c., and is also formed by heating *β -naphthaquinoneoxime dibromide* or *bromo- β -naphthaquinoneoxime* with concentrated hydrochloric or acetic acids. When this is treated with aqueous sulphurous acid, it is converted into *bromonaphthaquinol*; this crystallises in yellow needles, melts at 193°, and is reconverted into the quinone by oxidation with chromic acid. The quinone, when treated with soda or alcoholic ammonia, gives the known bromohydroxynaphthaquinone (m. p. 196·5°), and with aniline yields *β -bromo- β -anilido- α -naphthaquinone*, thus entirely differing from Zincke's *β -bromo- β -naphthaquinone*.

Naphtha- α -quinone- β -oxime dibromide, obtained by the action of bromine on naphtha- α -quinone- β -oxime, forms grey plates, melts at 154—155°, and is more stable than its isomeride. The corresponding *β -bromonaphtha- α -quinone- β -oxime*, [$\text{O} : \text{NOH} : \text{Br} = 1 : 2 : 3$], separates from alcohol in yellow, from acetic acid in dark-brown crystals, melts at 175°, and is soluble in alcohol, chloroform, acetic acid, benzene, ether, light petroleum and sulphuric acid, with brown colour, and in alkalis with orange colour.

β -Dibromo- α -naphthaquinoneoxime is obtained by the bromination of naphtha- α -quinone- α -oxime in either hot or cold acetic acid, an additive

compound seeming not to be formed; it crystallises in white needles, melts at $174-175^{\circ}$, and is soluble in the usual solvents except light petroleum and carbon bisulphide. A. J. G.

Action of Monamines on the Naphthaquinoneoximes. By C. BRÜMME (*Ber.*, **21**, 391—395).—Anilidonaphthaquinonanilide is formed when either of the three naphthaquinoneoximes is treated with aniline and glacial acetic acid. The mother-liquor contains a violet, crystalline substance, which melts at 260° . *Dinitroanilidonaphthaquinonanilide*, $C_{22}H_{14}N_2O(NO_2)_2$, is a reddish-brown, crystalline substance, which melts at 143° and is sparingly soluble in alcohol.

Paratoluidonaphthaquinoneparatoluidide, $C_{24}H_{20}N_2O$, forms long, red needles, and melts at 183° . The ψ -cumidine-derivative melts at 181° . The α -naphthylamine-derivative melts at 178° .

Anilidonaphthaquinonanilide, when heated with alcoholic hydrogen bromide or ethyl bromide, is converted into aniline and anilidonaphthaquinone. A. J. G.

β -Naphthylamine- δ -sulphonic Acid and β -Naphthylamine-sulphonic Acid F. By H. ERDMANN (*Ber.*, **21**, 637—639).—The author confirms the identity of these acids. The diazo-compounds prepared from them show complete identity in every particular, and when heated with phosphoric chloride, both acids yield Cleve's δ -dichloronaphthalene. A. J. G.

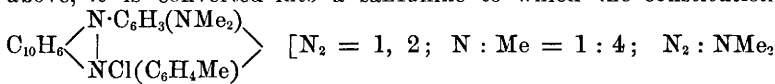
Eurhodines and Saffranines. By O. N. WITT (*Ber.*, **21**, 719—725).—*Dimethylnaphtheurhodine*, $C_{10}H_6 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ | \\ \text{N} \end{array} C_6H_3 \cdot NMe_2$ [$N_2 = 1, 2$;

$N : NMe_2 = 1, 2 : 4$], is prepared by heating 20 grams of nitroso-dimethylaniline hydrochloride (3 mols.), 10 grams of β -naphthylamine (2 mols.), and 50 c.c. of glacial acetic acid in a capacious flask; the reaction commences below 100° , and the yield is the better the more slowly it is conducted. When the reaction is complete, the thin melt is poured into boiling water acidified with hydrochloric acid, and precipitated with sodium acetate; the brownish-red mass is dissolved in alcohol acidified with hydrochloric acid, the solution evaporated to a small bulk and mixed with concentrated hydrochloric acid, when the hydrochloride separates in copper-brown needles. From this, the free base is obtained by treatment with aqueous ammonia; it forms large, well-formed, rhombic tables, red by transmitted, and red or green, according to the faces, by reflected light; it melts at 205° , sublimes in woolly flocks, dissolves in alcohol, ether, and the benzene hydrocarbons to yellow solutions with splendid yellow fluorescence. The solution in concentrated sulphuric acid is violet-red, and on dilution with water becomes successively black, green, grey, and bluish-violet. The salts are readily crystalline, have a bronzy lustre, and are dissociated by water. Dimethylparaphenylenediamine seems to be formed as a bye-product in the preparation.

Phenylnaphthylamine, when treated in like manner, yields a new dye which crystallises in black needles of metallic lustre, is soluble in water, is not precipitated by moderate addition of alkalis, and forms

a sparingly soluble nitrate. The aqueous solution is decolorised by zinc-dust, but reoxidises on exposure to air. Satisfactory numbers could not be obtained on analysis.

When paratolyl- β -naphthylamine is treated in the manner described above, it is converted into a saffranine to which the constitution



$= 1, 2 : 4]$ is assigned. This crystallises in long, very slender needles of violet-metallic lustre, and like all saffranines is very hygroscopic and difficult to burn. It dissolves in water with bluish-violet colour, and dyes fibres violet; soda precipitates the free base in red flocks, soluble in alcohol with red colour and splendid orange-red fluorescence. The nitrate is so insoluble that the most dilute solution of the dye seems to be completely precipitated by addition of a drop of nitric acid. The platinochloride is at first obtained as an insoluble, gelatinous precipitate, which, on short digestion on the water-bath, changes into a heavy, crystalline powder, consisting of black, lustrous needles. A nitro-derivative was obtained in red crystals.

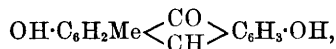
In this experimental evidence of the close relationship of an eurhodine and a saffranine-dye, the author sees a new proof of the correctness of the constitutional formulæ assigned by him to the saffranines.

A. J. G.

Naphthalene-derivatives. By O. N. WITT (*Ber.*, **21**, 726—728).—*Diparatolyldinaphthylamine*, $\text{C}_{20}\text{H}_{12}(\text{NH} \cdot \text{C}_6\text{H}_4\text{Me})_2$, is obtained by heating 10 grams of paratolynaphthylamine, 4 grams of nitrosodimethylaniline hydrochloride, 10 grams of zinc chloride, and 100 c.c. of glacial acetic acid on the water-bath. It forms lustrous, white crystals, melts at 224 — 225° , distils at higher temperatures with partial decomposition, and is dissolved by nearly all solvents. It does not give a picric acid compound, but gives a grass-green coloration with nitrous sulphuric acid. The nitroso-compound must be regarded as playing no part in the reaction beyond that of an oxidising agent, and may be replaced, although with diminished yield, by ferric chloride. An acetyl-compound was obtained, melting at 225° . When heated with hydrochloric acid at 220° , it is converted into paratoluidine and a resinous substance which can be obtained crystallised in needles melting at 193° .

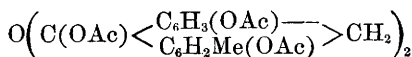
A. J. G.

Leuco-compounds from the Anthraquinone-dyes. By C. LIEBERMANN (*Ber.*, **21**, 435—446).—*Chrysophanhydranthron*,



is prepared by heating to boiling chrysophanic acid with 15 times its weight of glacial acetic acid and three times its weight of tin, and then adding fuming hydrochloric acid in small portions, until the original deep yellow colour has changed to pale yellow, and the whole of the chrysophanic acid has dissolved. The product is filtered whilst boiling, precipitated with water, and recrystallised from benzene. It is also formed by reducing chrysophanic acid with zinc-dust and

ammonia. It forms pale-yellow, microscopic plates, melts at 200—206°, and dissolves with difficulty in alkalis, the solution having a yellow colour and green fluorescence. The solution absorbs oxygen from the air, chrysophanic acid being reformed. It yields a peculiar acetyl-derivative, for which the constitution



is suggested; this forms microscopic, yellowish-white plates, melts at 230—231°, and is readily soluble in acetic acid, sparingly in alcohol, and so closely resembles acetylchrysarobin that it was at first mistaken for it; the substances are, however, distinguished by their behaviour on hydrolysis with sulphuric acid, each yielding its parent substance.

Flavopurpuranthranol, $\text{OH}\cdot\text{C}_6\text{H}_3 < \begin{array}{c} \text{C}(\text{OH}) \\ | \\ \text{CH} \end{array} > \text{C}_6\text{H}_2(\text{OH})_2$, obtained by

the reduction of flavopurpurin in the manner described above, forms clear yellow needles readily soluble in alcohol, acetone, and acetic acid, sparingly in benzene, soluble in alkalis with yellowish-brown colour and greenish fluorescence. By acetylation, a tetracetyl-compound is formed. On account of the instability of the anthranol, an attempt was made to combine the reduction with acetylation. This method has proved of great use, where, from their instability, the leuco-compounds are very difficult to prepare. Flavopurpurin (1 part), sodium acetate (2 parts), zinc-dust (3 parts), and acetic anhydride (10 to 15 parts), are boiled together for a few minutes, cooled, thrown into much water, and left for some hours; the precipitate is then extracted with boiling acetic acid, when two products are obtained; a pentacetyl-derivative, $\text{OAc}\cdot\text{C}_6\text{H}_3\cdot\text{C}_2(\text{OAc})_2\cdot\text{C}_6\text{H}_2(\text{OAc})_2$, which crystallises in nearly colourless, yellow plates, and melts at 239—240°, and the tetracetyl-compound already mentioned, which forms nearly colourless flocks, and melts at 107—105°.

Anthrapurpuranthranol, $\text{C}_{14}\text{H}_6(\text{OH})_4$, prepared by the reduction of anthrapurpurin, forms leather-yellow, microscopic needles, and yields a tetracetyl-derivative crystallising in needles and melting at 167°.

Anthragalanthranol, $\text{C}_{14}\text{H}_{10}\text{O}_4$, from anthragallo, crystallises in yellowish needles, does not show a definite melting point, and yields a triacetyl-derivative which melts at 203—205°. When an alkaline solution is exposed to the air, it assumes a beautiful violet colour, and on acidifying violet flocks separate, consisting of *anthragalhydroxyanthranol*, $\text{C}_6\text{H}_4\cdot\text{C}_2(\text{OH})_2\cdot\text{C}_6\text{H}_2(\text{OH})_2$.

Anthraflavanthranol, $\text{C}_{14}\text{H}_{10}\text{O}_3$, obtained by the reduction of anthraflavic acid, forms small, white needles. Its triacetyl-derivative crystallises in white needles, and melts at 165°.

Rufigalanthranol was only obtained as its heptacetyl-derivative, $\text{C}_{14}\text{H}_3(\text{OAc})_7$; this crystallises in pale-yellow needles. All these acetyl-derivatives show a characteristic fluorescence in alcoholic solution.

It is thus seen that the anthraquinone-dyes yield leuco-compounds on reduction. Although the evidence is not yet quite conclusive, it

would seem that anthragallol, flavopurpurin, anthrapurpurin, and anthraflavic acid yield anthranols, whilst chrysophanic acid, alizarin, and isanthraflavic acid yield the isomeric hydroanthranons.

When indigo is simultaneously reduced and acetylated, acetyl-indigo-white, $C_{15}H_{10}N_2O_2Ac_2$, is obtained in nearly white needles, which melt at 226° , and are pretty stable. A. J. G.

Terpenes and their Derivatives. By J. W. BRÜHL (*Ber.*, **21**, 457—477).—A continuation of the author's former paper on this subject (this vol., p. 377), in which the oxygen-derivatives of the terpenes are discussed. The physical properties of these are arranged in a table similar to that given in the case of the terpenes.

Menthol, $C_{10}H_{20}O$, is probably a derivative of menthene, with which it occurs in peppermint oil. It is laevorotatory, and its molecular refraction shows that it contains no double bond, and that its oxygen is united by single affinities. It is a secondary alcohol, and on oxidation yields the dextrorotatory menthone, $C_{10}H_{18}O$, a ketone the relation of which to menthol is similar to that of camphor, $C_{10}H_{16}O$, to borneol, $C_{10}H_{18}O$. By the action of hydrogen chloride, menthol is converted into the compound $C_{10}H_{19}Cl$. This, by loss of HCl, yields hydromenthene, $C_{10}H_{16}$, from the tetrabromide of which, by the removal of 4 mol. HBr, paracymene is obtained. Menthol is probably hydroxyhexahydroparacymene, $[Pr : OH = 1 : 3]$.

Cineole, $C_{10}H_{18}O$, contains neither hydroxyl nor carbonyl, and yields, by loss of water, dipentene and also paracymene. It can form very unstable additive compounds, but according to its molecular refraction is a saturated compound. It is optically inactive, and optically inactive dipentene dihydrochloride is formed when hydrogen chloride is passed into warm cineole. Of the nine possible formulæ for cineole

as a paracymene-derivative, only one, $CPr \begin{array}{c} \diagup CH_2 \cdot CH_2 \diagdown \\ \diagdown O \diagup \\ \diagup CH_2 \cdot CH_2 \diagdown \end{array} CMe$, is in

keeping with these facts.

Terpin, $C_{10}H_{20}O_2$, is an optically inactive compound formed by the action of alcoholic nitric acid on pinene. It is a saturated compound containing two hydroxyl-groups. By the action of hydrogen chloride on terpin, a compound, $C_{10}H_{18}Cl_2$, is formed, identical with the additive-product from dipentene and hydrogen chloride. Boiled with dilute mineral acids, terpin is first converted into terpineol, $C_{10}H_{18}O$, and then into dipentene. Terpineol contains one hydroxyl-group, has one double bond, and is optically active. In all probability terpin is a dihydroxy-, terpineol a monohydroxy-derivative of dipentene.

Camphor, $C_{10}H_{16}O$, probably also a derivative of the terpenes and paracymene, as it is easily obtained from camphene. From the molecular refraction of ethylcamphor, it is concluded that camphor contains no double bond. Borneol, the secondary alcohol derived from camphor, is also a saturated compound. From bornyl chloride, $C_{10}H_{17}Cl$, by elimination of HCl, camphene is obtained, so that borneol like camphor appears to be related to that terpene.

Isomeric with camphor are myristicol and absinthole. The first of these is an alcohol, and contains two double bonds. By the action of

phosphorus chloride a compound $C_{10}H_{15}Cl$ is obtained, which on elimination of HCl yields paracymene. Myristic acid is, therefore, probably a phenol of hydrated paracymene. Of absinthol but little is known; it is neither an aldehyde nor a ketone, but the oxygen is probably combined as in cineole.

Carvole and carvacrol, $C_{10}H_{14}O$. The molecular refraction is found to support Goldschmidt's views of the relation these substances bear to one another (Abstr., 1887, 475).

Safrole, $C_{10}H_{10}O$, contains according to the molecular refraction four double bonds, and from what is known of its chemical behaviour has most probably the constitution $C_3H_5 \cdot C_6H_5 \cdot \begin{smallmatrix} O \\ < \\ O \end{smallmatrix} CH_2$. The recently discovered shikimole appears to be identical with safrole. Both are optically inactive. H. C.

Action of Formic Acid on French Terebenthene. By J. LAFONT (*Compt. rend.*, 106, 140—142).—The terebenthene boiled at $155\text{--}158^\circ$; rotatory power, $[\alpha]_D = -39^\circ 50'$.

2 parts of terebenthene and 1 part of glacial formic acid are gradually mixed, care being taken to avoid a rise of temperature, and the mixture is allowed to remain at the ordinary temperature for some time. Its rotatory power increases considerably. It is then treated with water, and fractionated. The fraction boiling at $135\text{--}138^\circ$, under a pressure of 40 mm., is more mobile than the original terebenthene; rotatory power, $[\alpha]_D = -69^\circ 25'$; sp. gr. at $0^\circ = 0.9986$. It has the composition $C_{10}H_{16}, CH_2O_2$, and with dry hydrogen chloride yields formic acid and terpinene hydrochloride. It is violently attacked by nitric acid with formation of resinous products. Potash produces potassium formate and a viscous substance identical with the terpinols obtained by the action of acetic acid on caoutchouc and terebenthene. The rotatory power of this terpinol is $[\alpha]_D = -80^\circ$, and it melts at 32° .

The fractions boiling above 145° in a vacuum contain *terpin formate*, $C_{10}H_{16}(CH_2O_2)_2$, which boils at $170\text{--}180^\circ$ and yields potassium formate and terpin when treated with alcoholic potash, besides a viscous, yellowish diterpene which boils at $205\text{--}215^\circ$; sp. gr. at $0^\circ = 0.9446$; rotatory power, $[\alpha]_D = -14^\circ 15'$.

The first fractions of the original product contain terebenthene with a slightly increased rotatory power, $[\alpha]_D = -41^\circ 32'$, and a mixture of cymene with terpinene boiling at about 178° . In this respect, the action of formic acid is identical with that of acetic acid.

When terebenthene and formic acid in the same proportions are heated in sealed tubes at 100° for 12 hours, treated with water and fractionated, the main product is diterpene, a viscous, yellowish, optically inactive substance which boils at $205\text{--}215^\circ$, under a pressure of 40 mm.; sp. gr. at $0^\circ = 0.9404$. The first fractions contain terpinene and cymene, with possibly a small quantity of camphene formate.

The formation of terpinene formate by the action of formic acid on terebenthene at the ordinary temperature is remarkable, since this

compound is not formed by the action of formic acid on terpinele itself.
C. H. B.

Yield of Essential Oils by Drugs and Plants. (*Pharm. J. Trans.* [3], 18, 363.)—A table of the percentages of essential oils yielded by 159 species of plants.
R. R.

Camphorimide. By A. GUARESCHI (*Chem. Centr.*, 1887, 1354—1355; from *Ann. Chim. Farm.*, 87, 113—122).—A good yield of camphorimide is obtained by heating camphoric acid with 0·3 part of carbamide at 110—120° and finally at 120—125°.

Moine obtained camphorimide and allylcamphorimide by the action of camphoric acid on allylthiocarbamide. Camphoric acid and thiocarbamide, or ammonium, or potassium thiocyanate, when fused together, likewise give camphorimide. When potassium thiocyanate is used, carbon oxysulphide is formed.

The camphorimide obtained by these reactions is identical with Laurent's camphorimide from ammonium camphoramate. The specific rotation of a solution of camphorimide in chloroform is $[\alpha]_D = -10\cdot6^\circ$. A silver compound, $C_8H_{14}C_2O_2\cdot NAg$, was formed.

Camphorchlorimide, $C_8H_{14}\begin{smallmatrix} CO \\ < \\ CO \end{smallmatrix}NCl$, was obtained by dissolving 1 gram of camphorimide in 100 parts of water, adding 1 c.c. of acetic acid, and 10 c.c. of concentrated solution of bleaching powder. From weak alcohol, it crystallises in colourless needles melting at 115·5°. With paratoluidine and aniline, the chlorimide gives a violet-red, with diphenylamine, a green, with pseudocumidine, an orange-coloured product.
J. P. L.

Phycophæin. By F. SCHÜTT (*Chem. Centr.*, 1887, 1379—1380; from *Ber. Bot. Ges.*, 5, 259—274).—Phycophæin obtained from the various Phæophyceæ (*Fucaceæ*) is identical in composition. The optical properties of phycophæin consist of a uniform increase of absorption from the red to the blue end of the spectrum. As there are no absorption-bands, the curve is the chief characteristic.

Phycophæin is easily soluble in hot water, slightly soluble in dilute alcohol, insoluble in ether, carbon bisulphide, benzene, light petroleum, and fixed oils. It is more or less completely precipitated by acids, partially precipitated by soda, and not at all by ammonia or salts of the alkalis. It is precipitated by the salts of the alkaline earths, &c. From its chemical and optical properties, it must, at present, be assigned a position by itself, as it is not directly connected with chlorophyllin or any of the green colouring matters of the chlorophyll-group.
J. P. L.

Cyclamin. By G. MICHAUD (*Chem. Centr.*, 1887, 1397; from *Arch. Sci. Phys. Nat.* [3], 18, 198—212).—1 part of cyclamin in 6000 parts of water causes frothing, and in this respect cyclamin surpasses saponin. Cyclamin is more soluble in water at the ordinary temperature than at 70°, but above this temperature the solubility again increases, until at 100° it is about the same as at the ordinary

temperature. The rotatory power of cyclamin cannot be determined in watery solution on account of opalescence; in alcoholic solution the author found $[\alpha]_D = -11.40^\circ$. Sachsse states that the rotatory power is -15.10° . Mineral acids decompose cyclamin into cyclamiretin and a sugar. The author assigns the formula $C_{36}H_{56}O_{18}$ to cyclamin.

Cyclaminic acid, $C_{36}H_{56}O_{19}$, a weak acid insoluble in water, but easily soluble in alcohol, results from the action of chlorine on a watery solution of cyclamin.

Nitric acid converts cyclamin, cyclamiretin, or cyclaminic acid into *chrysolin*, a nitrogenous, amorphous, and feebly acid substance of the formula $C_{15}H_{21}O_6N$.
J. P. L.

Tyrotaxon. By V. C. VAUGHAN (*Pharm. J. Trans.* [3], 18, 479—480).—If milk to which some butyric acid ferment has been added, is kept in closely stoppered bottles for eight or ten days, then filtered, and the filtrate, after neutralisation with sodium carbonate, extracted with ether, tyrotaxon will be obtained in considerable quantity. When a solution in alcohol to which some platinum chloride has been added is evaporated on the water-bath, a violent explosion takes place. The author finds that in this respect tyrotaxon agrees with diazobenzene compounds, as it does also in giving a similar precipitate with gold chloride. Diazobenzene butyrate and tyrotaxon were in fact found to be identical in their chemical behaviour and in their physiological effects (described at length in the paper); and from tyrotaxon obtained from milk, diazobenzene potassium hydroxide, was obtained according to Griess' method. Diazobenzene or some closely-allied substance will probably be found in all those foods which, after putrefactive changes, produce nausea, vomiting and diarrhoea.

Milk or other liquid to be tested for this poison should be kept in well-stoppered bottles, for exposure of the liquid to the air may decompose the tyrotaxon in a few hours. The filtrate from the milk, or the filtered aqueous extract of cheese, should be neutralised with sodium carbonate, shaken with half its volume of pure ether, and time given for the complete separation. Pure tyrotaxon being insoluble in ether, the substance probably owes its solubility at this stage to the presence of impurities. The ether is then separated and allowed to evaporate spontaneously, after which the residue may be dissolved in distilled water, and again extracted with ether. A drop of an aqueous solution of the ether residue is then added to a mixture of phenol and pure sulphuric acid, three drops of each, on a porcelain plate, when a coloration, orange-red to purple, will be produced if tyrotaxon be present. To the remainder of the aqueous solution, an equal volume of saturated aqueous potash is added, and the mixture evaporated on the water-bath. The double hydroxide of potassium and diazobenzene will be formed if tyrotaxon be present, and may be separated in beautiful six-sided plates, soluble in absolute alcohol, from which it may be precipitated by ether.
R. R.

Diastase. By C. J. LINTNER (*J. pr. Chem.* [2], 36, 481—498; compare *Abstr.*, 1887, 165).—The author has found that diastase

prepared from maize by digestion with water, precipitation with alcohol, and subsequent purification by alternately dissolving in water and precipitating with alcohol, has the same diastatic activity and contains the same quantity of nitrogen (10.4 per cent.) as that obtained from barley. Loew's method of purification by precipitation with lead acetate is unsatisfactory, as thereby the diastase loses six-sevenths of its activity. The presence of small quantities of the chlorides of sodium, potassium, and calcium in no way affects the action of diastase on starch solution, but if these substances be present in considerable quantities the conversion into sugar is retarded. Acids and alkalis, cupric sulphate, and probably most salts of the heavy metals, either diminish or completely destroy the activity of diastase. There is at present no evidence to show that two ferments exist in malt, one of which is capable of dissolving starch, whilst the other converts it into sugar; and it must be provisionally accepted that diastase has both these properties. A convenient method of preparing pure maltose consists in treating a solution of starch at ordinary temperatures with precipitated diastase.

G. T. M.

Pyrrolidine. By F. C. PETERSEN (*Ber.*, **21**, 290—293).—The author has purified the pyrrolidine prepared by Ladenburg's method, (*Abstr.*, 1887, 499), by converting it into the bismutho-iodide and decomposing this by distillation with aqueous soda. Thus prepared, pyrrolidine boils at 86.5—88° (compare *Abstr.*, 1885, 1243) and has a specific gravity = 0.879 at 0° and = 0.871 at 10°. The *cadmio-iodide*, $2(C_4NH_5, HI), CdI_2$, crystallises from water in colourless, tabular scales and melts at 200—202°. The nitroso-derivative, $C_4NH_5 \cdot NO$, is an oil which distils at 214° with partial decomposition and is readily soluble in water.

W. P. W.

β -Picoline. By F. BACHÉR (*Ber.*, **21**, 293—294).—The determinations of the boiling point of β -picoline prepared by Stoehr (this vol., p. 63) and by Hesekeiél (*Abstr.*, 1885, 812), do not agree. The author has purified the base obtained by Hesekeiél's method by digestion in hydrochloric acid solution with sodium nitrite on a water-bath, and conversion into and crystallisation of its mercuriochloride. The base, however, boiled chiefly at 140—142° (corr. 142—144°), whilst fractional crystallisation of the platinochloride prepared from the residue in the distilling flask gave four fractions melting at 187—191°, and corresponding with Stoehr's description of the salt. The research is being continued.

W. P. W.

γ -Picoline and γ -Pipicoline. By A. LADENBURG (*Ber.*, **21**, 285—289).—A commercial lutidine (b. p. = 143—160°) was found to contain 2:4 lutidine, β -picoline, and γ -picoline, and the latter was separated from it by the following method. The fraction distilling at 143—147° was converted into the platinochloride, which was washed with ether-alcohol, dissolved in sufficient water to form a 3 per cent. solution, and boiled for many hours in a reflux apparatus in order to convert the picolines into the sparingly soluble, yellow, crystalline platino-salts: the lutidine platinochloride is not affected by this treatment. The platino-salts were then converted

into platinochlorides by digestion with concentrated hydrochloric acid in a current of hydrogen chloride, and the γ -salt purified by crystallisation.

γ -Picoline boils at 142.5 — 144.5° (corr.) and has a sp. gr. = 0.9742 at 0° ; the platinochloride melts at 231° with decomposition; the aurochloride forms beautiful, lustrous prisms and melts at 205° ; the picrate melts at 167° , and the mercurochloride melts at 128 — 129° .

γ -Pipicoline, $C_6H_{13}N$, was obtained by the action of sodium on a boiling alcoholic solution of γ -picoline. It is a colourless, hygroscopic liquid which boils at 126.5 — 129° (corr.) and has a sp. gr. = 0.8674 at 0° . It fumes strongly in the air, has a piperidine-like odour, and is readily soluble in water. The hydrochloride is crystalline and readily soluble in water; the platinochloride, $(C_6NH_{13})_2, H_2PtCl_6$, crystallises in lustrous prisms, melts at 203° with decomposition, and is soluble in water; the aurochloride crystallises in lustreless, yellow needles, melts at 125 — 127° and is sparingly soluble in water; the cadmio-iodide forms white scales and melts at 135° ; the bismutho-iodide crystallises in characteristic red forms, and the picrate and mercurochloride are crystalline.

The specific gravity of pyridine prepared from the mercurochloride is stated to be 1.0033 at 0° , and a number of instances are cited in which the difference between the molecular volumes of an alkylated pyridine and its hydrogenated derivative approximates to that required by Horstmann's law (Abstr., 1887, 545). W. P. W.

Constitution of Aldehydecollidine. By E. DÜRKOPF and M. SCHJAUGK (*Ber.*, **21**, 294—299).—A comparison between isocinchomeric acid and the dicarboxylic acid obtained as the final product of the oxidation of aldehydecollidine has established their complete identity, and inasmuch as the collidine has been shown to yield α -picoline (Abstr., 1887, 737), there can be no doubt that its constitution is expressed by the formula C_6NH_3MeEt [$Me : Et = 2 : 5$]. To explain the formation of this compound from aldehyde and aldehyde-ammonia, the authors suggest that a molecule of aldehyde and a molecule of aldehyde-ammonia react to form the compound $CHO \cdot CH : CHMe, NH_3$, that simultaneously condensation of the aldehyde and formation of crotonaldehyde also ensues, and that these two products interact under the conditions of the experiment to form aldehydecollidine with the loss of 2 mols. of water. The fractions of lower-boiling point obtained in the purification of aldehydecollidine contain a noteworthy amount of α -picoline, and a small fraction boiling at 160 — 165° seems to contain β -ethylpyridine, but this is not absolutely certain. W. P. W.

Pseudoquinolineanitrile. By E. LELLMANN and H. REUSCH (*Ber.*, **21**, 397—401).—It has previously been pointed out that quinolineanasulphonic acid and quinolineanacarboxylic acid exist in two modifications (Lellman, Abstr., 1887, 973; Lellmann and Lange, *ibid.*, 737). The authors have now prepared the second modification of the nitrile, the intermediate product. *Pseudoquinolineanitrile*, C_9NH_5CN , is obtained by distilling the pseudosulphonic acid

with potassium cyanide. It crystallises in slender, colourless needles with $1\frac{1}{2}$ mol. H_2O and melts at 70° . When exposed to air, it loses 1 mol. H_2O and then melts at 74.5° ; the remainder of the water is lost on drying over sulphuric acid; the anhydrous substance melts at 89° . It would thus seem that this substance differs from Bedall and Fischer's ananitrile (Abstr., 1882, 413) which presumably is anhydrous (as no reference is made to its containing water of crystallisation) and yields the other modification of the anacarboxylic acid on hydrolysis. Other cases of the existence of these modifications of ana-derivatives are referred to, and further work on the subject is in progress. A. J. G.

Thio-derivatives of Quinoline. By J. ROOS (*Ber.*, 21, 619—630).— *α -Quinolyl mercaptan* (*α -thioquinoline*) $\text{C}_9\text{NH}_7\text{SH}$ [$\text{SH} = 2'$] is prepared by heating carbostyryl and phosphoric sulphide at 135 — 145° ; it forms yellow plates, melts at 174° , is insoluble in cold, sparingly soluble in hot water, readily soluble in alcohol, ether, benzene, chloroform, carbon bisulphide, and acetic acid. It shows both acid and basic properties and readily forms double salts; it has tinctorial properties, but is not a sufficiently powerful dye for technical purposes. Neither hydroxylamine nor phenylhydrazine react with it.

α -Quinolyl disulphide, $(\text{C}_9\text{NH}_7)_2\text{S}_2$, is obtained by oxidising the mercaptan with hydrogen peroxide; it crystallises in lustrous, white plates, melts at 137° , and is insoluble in alkalis, ammonia, and water, readily soluble in acids and in alcohol, ether, benzene, light petroleum, and chloroform.

α -Quinolyl ethyl sulphide, $\text{C}_9\text{NH}_7\text{SEt}$, is prepared by the action of ethyl iodide on equimolecular proportions of quinolyl mercaptan and sodium dissolved in alcohol, as an uncrystallisable oil which cannot be distilled; it was therefore converted into the *platinochloride*, which crystallises in microscopic octahedrons with 1 mol. H_2O . The *hydriodide*, $\text{C}_9\text{NH}_7\text{SEt}\cdot\text{HI}$, is formed by heating the mercaptan with ethyl iodide; it forms pale-yellow crystals and melts at 154° .

γ -Methylquinolyl mercaptan (*α -thiolepidine*), $\text{C}_9\text{NH}_7\text{Me}\cdot\text{SH}$ [$\text{SH} : \text{Me} = 2' : 4'$], prepared by heating γ -methylcarbostyryl with phosphoric sulphide at 140 — 150° , crystallises in pale-yellow needles, melts at 253° , sublimes at a higher temperature in yellow needles, and is insoluble in water, sparingly soluble in cold alcohol, readily in ether, benzene, chloroform, and carbon bisulphide. It has both acid and basic properties and does not react with hydroxylamine or phenylhydrazine. The *disulphide*, $(\text{C}_9\text{NH}_7\text{Me})_2\text{S}_2$, prepared by oxidation with hydrogen peroxide, forms white plates, melts at 167° , and is readily soluble in alcohol, ether, and benzene, insoluble in alkalis.

γ -Methylquinolyl ethyl sulphide, $\text{C}_9\text{NH}_7\text{Me}\cdot\text{SEt}$, is an oil; the *platinochloride* crystallises with $\frac{1}{2}$ mol. H_2O . The *hydriodide*, obtained by the action of ethyl iodide on the mercaptan, forms long, yellow needles and melts at 214° .

α -Methylquinolyl mercaptan (*γ -thioquinaldine*), $\text{C}_9\text{NH}_7\text{Me}\cdot\text{SH}$ [$\text{SH} : \text{Me} = 4' : 2'$], is prepared from γ -oxyquinaldine; it crystallises with 1 mol. H_2O in yellow prisms, which soon turn red on exposure

to air, melts at 187° , and is sparingly soluble in cold, moderately soluble in hot water and in alcohol, ether, and benzene.

α -Methylquinolyl ethyl sulphide, $C_{10}NH_8SEt$, prepared like the corresponding compounds, crystallises in well-formed, white needles, melts at 56° , is readily soluble in alcohol and ether, insoluble in water, and gives a crystalline platinochloride. A. J. G.

Action of Sulphuric Acid on Quinoline. By G. V. GEORGIEVICS (*Monatsh. Chem.*, **8**, 639—646; compare this vol., p. 296).—When orthoquinolinesulphonic acid is heated with sulphuric acid (7 parts) at 300° for eight hours, paraquinolinesulphonic acid is formed. The yield is 70 per cent. Quinoline is formed as intermediate product.

Orthoquinolinesulphonic acid is obtained when quinoline is heated with sulphuric acid at 220 — 230° ; if the temperature is raised to 240 — 250° , the para-acid is formed.

Paraquinolinesulphonic acid crystallises in long monoclinic needles; $a : b = 1.3514 : 1$; $\beta = 66^{\circ} 46' 26''$.

Parasulphocinchonic acid (Weidel, *Abstr.*, 1882, 225) is conveniently prepared by heating cinchonic acid with sulphuric acid (6 to 7 parts) at 290 — 300° for 8 to 10 hours. The whole is poured into water and about three-fourths of the sulphuric acid precipitated with barium carbonate. It is then filtered, extracted with boiling water, and the united filtrates evaporated until a sample of the liquid deposits crystals in one or two hours; after standing 24 hours, these are collected and recrystallised two or three times. The yield of pure acid is more than 40 per cent. of that required by theory. When the acid is fused with potash, a hydroxy-acid is formed identical with that obtained by Weidel (*loc. cit.*), and also with Skraup's xanthoquinic acid (*ibid.*, 223). N. H. M.

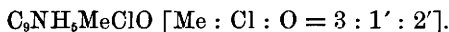
Action of Hypochlorous Acid on Quinoline and its Derivatives. By A. EINHORN and R. LAUCH (*Annalen*, **243**, 342—362).—Pseudochlorocarbostryl, C_9H_6NOCl , formed by the action of hypochlorous acid on quinoline or of a solution of bleaching powder on quinoline borate, has been previously described by the authors (*Abstr.*, 1886, 370). The chlorine-atom in this compound is easily displaced by hydrogen, yielding carbostyryl, but it could not be displaced by groups of atoms. The substance is converted into an isomeride, by the action of absolute alcohol at 100° , or by heating it to a temperature a few degrees above the melting point. The new compound forms rhombic plates and melts at 262 — 263° ; its chlorine-atom cannot be eliminated by the action of moist oxide of silver or by nascent hydrogen. It forms a crystalline potassium salt, and yields chlorisatin on oxidation. As the same compound is formed from 3-chloroquinoline and the same chloroisatin from 3.1' chlorhydroxyquinoline, it is evident that in the intramolecular change which has taken place, the chlorine-atom in the original compound has migrated from the pyridine-ring to the benzene nucleus, forming *parachlorocarbostryl*. A third isomeride resembles the preceding compound, but melts at 106° .

Parachlorocarbostryl hypochlorite, $C_9NH_5Cl \cdot OCl$ [$Cl : OCl = 3 : 1'$], is formed by the action of bleaching powder solution on a solution of

parachlorocarbostryl. It is deposited from an acetic acid solution in plates melting at 115°. On exposure to the air, the crystals lose their lustre and the melting point of the substance rises. The substance is deposited from water or ethyl acetate in needles, and melts at 145°. It is much more stable than pseudochlorocarbostryl, but is decomposed by boiling alkalis, forming parachlorocarbostryl.

Anachlorocarbostryl hypochlorite, prepared from metachloroquinoline, crystallises in needles and melts at 155°. It is decomposed by boiling solutions of alkalis, yielding anachlorocarbostryl, melting at 287°.

Paramethylquinoline yields methylpseudochlorocarbostryl,



This substance melts with decomposition at 120·5°. An intramolecular change takes place when it is dissolved in boiling alcohol, the chlorine-atom migrating to the benzene nucleus, forming methyl chlorocarbostryl.

These results show that quinoline and 3-methylquinoline are converted into unstable pseudochlorocarbostryls, but ana- and parachloroquinoline yield hypochlorites. Orthochloroquinoline and orthomethylquinoline, under similar treatment, yield dichloro-substitution products.

W. C. W.

Action of Phosphorus Pentachloride on Aniline Ethylmalonate and on Orthotoluidine Ethylmalonate. By L. RÜGHEIMER and C. S. SCHRAMM (*Ber.*, 21, 299—307; compare Abstr., 1887, 738). Chlorethylhydroxyquinoline, $[\text{Cl} : \text{Et} : \text{OH} = 2' : 3' : 4']$, is converted into *ethylhydroxycarbostryl*, $[\text{OH} : \text{Et} : \text{OH} = 2' : 3' : 4']$, by heating with dilute hydrochloric acid at 165°. This is readily soluble in alcohol and acetone, and crystallises from acetic acid in lustrous, well-formed prisms, which lose their lustre on exposure to the air. The alcoholic solution is coloured a dark-yellow on treatment with ferric chloride.

Hydroxyethyltolucarbostryl, $[\text{OH} : \text{Et} : \text{OH} = 2' : 3' : 4']$, melts at 217·5—220° (not 222—223·5°), and is soluble in acetone and acetic acid. Ferric chloride imparts to its alcoholic solution a yellow colour rapidly changing to yellowish-red.

α-Dichlorobutyranilide, $\text{CEtCl}_2\text{CO}\cdot\text{NHPh}$, can be obtained from the product of the action of phosphorus pentachloride on aniline ethylmalonate by treating it with aqueous sodium carbonate in excess, heating cautiously on a water-bath, filtering and precipitating with hydrochloric acid. The precipitate is freed from chlorethylhydroxyquinoline by repeated treatment with concentrated hydrochloric acid, and the *α*-dichlorobutyranilide is purified by solution in aqueous sodium carbonate and subsequent precipitation with hydrochloric acid. It is a white powder which melts at 199—200°, and is converted into *α*-chlorhydroxybutyranilide-phenylcarbamine by distilling its solution in aqueous sodium carbonate nearly to dryness, adding the distillate to the contents of the flask, and again distilling, the process being repeated several times. Phenylcarbamine is formed during the operation. The author's view of the formation of *α*-chlorhydroxybutyranilide-phenylcarbamine is thus confirmed, and the

formula $\text{NPh}\cdot\text{CH}\cdot\text{O}\cdot\text{C}\cdot\text{EtCl}\cdot\text{CO}\cdot\text{NPh}$ is now ascribed to the compound. It is readily soluble in alcohol, less so in light petroleum, and yields phenylcarbamine when boiled with concentrated aqueous potash.

α -Chlorhydroxybutyro - orthotoluide - orthotolylcarbamine, probably $\text{C}_6\text{H}_5\text{Me}\cdot\text{N}\cdot\text{CH}\cdot\text{O}\cdot\text{C}\cdot\text{EtCl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, is obtained under similar conditions from the product of the action of phosphorus pentachloride on orthotoluidine ethylmalonate. It crystallises in needles, melts at $105\text{--}107^\circ$, is readily soluble in alcohol, less so in light petroleum, and when heated with sodium carbonate at 130° gives off the odour of phenylcarbamine.

W. P. W.

Synthesis of the Homologues of 4' Hydroxyquinaldine. By M. CONRAD and L. LIMPACH (*Ber.*, **20**, 523—533).—*Methyl orthotolylamidocrotonate*, $\text{C}_{12}\text{H}_{15}\text{NO}_2$, is prepared by keeping a mixture of orthotoluidine and methyl acetoacetate (eq. mols.) for a day; the water which separates is removed, and the oily product which afterwards solidifies is crystallised from alcohol, from which it separates in lustrous prisms melting at 31° . The *ethyl salt* is a slightly yellow oil.

Orthomethyl- γ -hydroxyquinaldine, $\text{C}_9\text{NH}_2\text{Me}_2\cdot\text{OH}$ [$\text{Me}_2 : \text{OH} = 1 : 2' : 4'$], is formed together with some orthoditolylcarbamide when ethyl tolylamidocrotonate is quickly heated at $240\text{--}250^\circ$. It crystallises from water, which dissolves it sparingly, in plates, with 1 mol. H_2O . The anhydrous substance melts at $260\text{--}261^\circ$, dissolves readily in alcohol, dilute acids, and alkalis, and is almost insoluble in ether, benzene, and chloroform. The *platinochloride* crystallises in light yellow, matted needles, becomes dark at 250° , decomposes completely at 270° , and is readily soluble in boiling water or alcohol.

Methyl paratolylamidocrotonate, $\text{C}_{12}\text{H}_{15}\text{NO}_2$, forms large, lustrous prisms melting at $60\cdot5^\circ$, and is readily soluble in ether and alcohol. The *ethyl salt* melts at $29\cdot5^\circ$.

Paramethyl- γ -hydroxyquinaldine, $\text{C}_{11}\text{H}_{11}\text{NO}$, obtained together with ditolylcarbamide by quickly heating the ethyl salt just mentioned, crystallises in needles with 1 mol. H_2O ; the anhydrous compound melts at $274\text{--}275^\circ$. The *hydrochloride* dissolves very readily in hot water and crystallises in slender needles; the *platinochloride* crystallises in orange-coloured, lustrous prisms which melt at 228° .

Orthoparadimethyl- γ -hydroxyquinaldine, $\text{C}_{12}\text{H}_{13}\text{NO}$, prepared by heating ethyl metaxylyl- β -amidocrotonate, crystallises in needles with 1 mol. H_2O , melts at $263\text{--}264^\circ$, and is readily soluble in alcohol, almost insoluble in ether and benzene. The *platinochloride* forms slender, pale-yellow needles, and melts at 282° with decomposition.

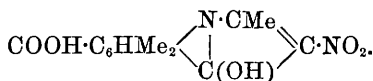
Orthoparadimethyl- γ -chloroquinaldine, $\text{C}_{12}\text{H}_{12}\text{NCl}$, is obtained by treating the hydroxy-derivative with phosphorus pentachloride in presence of phosphorus oxychloride, and afterwards heating the whole at 130° for $\frac{1}{2}$ hour. It crystallises from ether in flat prisms, almost insoluble in water, readily in dilute acids, in alcohol, ether, and benzene, melts at 114° , and boils at $297\text{--}298^\circ$. The *platinochloride* forms reddish-yellow needles, very sparingly soluble in hot water. When the base is heated with aniline for 10 minutes at 185° , *phenylamidodimethylquinaldine*, $\text{C}_9\text{NH}_2\text{Me}_2\cdot\text{NHPh}$ [$\text{Me}_2 : \text{NHPh} = 1 : 3 : 2' : 4'$], is formed;

this crystallises from hot dilute alcohol in prisms melting at 150° . Dixylylcarbamide, obtained in the preparation of dimethylhydroxyquinaldine, melts at 263° .

Methyl cumylamidocrotonate, $C_{14}H_{19}NO_2$, melts at 60.3° ; the *ethyl salt* is a viscous, oily substance which when heated at 250° yields condensation products; amongst them *dicumylcarbamide* melting above 300° .

Dicumylcarbamide, $C_{19}H_{24}N_2O$, which is contained in the volatile product obtained by heating ethyl cumylamidocrotonate, crystallises in white, lustrous needles melting above 300° ; it is insoluble in the usual solvents.

Trimethyl- γ -hydroxyquinaldine, $C_{13}H_{15}NO$ [$Me_4 : OH = 1 : 3 : 4 : 2' : 4'$], the non-volatile product obtained by heating methyl cumylamidocrotonate, crystallises in lustrous prisms which sublime at 285° with partial decomposition, but without melting. It is readily soluble in alcohol, sparingly soluble in water. The *platinochloride* separates from alcohol in lustrous prisms which decompose at above 275° without previous fusion. When the base is heated on a water-bath with 10 parts of nitric acid (sp. gr. = 1.4), a violent reaction takes place and a product is obtained which contains, among other substances, *nitrodimethylhydroxyquinaldinecarboxylic acid*,



This forms a fine white powder which decomposes at a high temperature without melting. The *sodium salt* crystallises (with 1 mol. H_2O) in long, slender, pale-yellow needles of a satiny lustre.

Ethyl α -naphthylamidocrotonate, $C_{16}H_{17}NO_2$, crystallises in white lustrous needles melting at 45° . When heated at 240° , a violent reaction takes place; the temperature rises to 280° and the whole solidifies.

α -Naphtho- γ -hydroxyquinaldine, $C_{14}H_{11}NO$, separates from its alcoholic solution in groups of needles which partly sublime but do not melt even at 300° . The *nitrate* is rather readily soluble in hot water; the *platinochloride* is a pale-yellow substance, very sparingly soluble in hot water.

Ethyl β -naphthylamidocrotonate, $C_{16}H_{17}NO_2$, crystallises in well-formed prisms melting at 66° , readily soluble in alcohol. When heated at 240° , it behaves similarly to the α -compound.

β -Naphtho- γ -hydroxyquinaldine, $C_{14}H_{11}NO$, crystallises in prisms which do not melt at 300° ; it is sparingly soluble in water, more soluble in alcohol. The *platinochloride* forms a bright yellow, very sparingly soluble precipitate. The constitution of β -naphthohydroxy-

quinaldine is probably $C_{10}H_6 \begin{array}{c} \diagup N \cdot CMe \\ | \\ \diagdown C(OH) \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} CH$ [$N : C \cdot OH = 1 : 2$].

N. H. M.

Syntheses in the Quinoline Series by means of Acetyl-acetone. By A. COMBES (*Compt. rend.*, 106, 142—145).—2' 4'

Dimethylquinoline is obtained by dissolving acetylacetoneanilide in concentrated sulphuric acid and heating for a short time on the water-bath. It boils without decomposition at 264—265°.

2'. 3'. 4' *Trimethylquinoline* is prepared by treating methylacetylacetoneanilide in a similar way. It melts at 65° and boils at 285°.

3. 2'. 4' *Trimethylquinoline* is obtained in the same way, from the derivative of acetylacetone and paratoluidine. It forms white crystals, melts at 39—40°, boils at 281—282° without decomposition, and yields a crystalline platinumchloride which melts at 220° without decomposing.

1. 2'. 4' *Trimethylquinoline* is obtained from the orthotoluidine-derivative in the same way. It boils at 280° and forms crystallisable salts. The platinumchloride melts without decomposition at 255—260°.

C. H. B.

Synthesis of 2' : 4' Phenylhydroxyquinoline. By M. CONRAD and L. LIMPACH (*Ber.*, 21, 521—522).—When ethyl benzoylacetate is heated for several days with aniline, *ethyl β-phenylamidophenylacrylate* is obtained as a thick oil, readily soluble in ether, alcohol, and benzene. This is quickly heated at 250° for a short time; alcohol and some other volatile products distil over, whilst the residue consists of 2' : 4' phenylhydroxyquinoline hydrochloride, from which the free base is liberated by means of sodium carbonate. It is identical with the compound prepared by Just (*Abstr.*, 1886, 811). It is probable that most of the 2' : 4' phenylhydroxyquinoline-derivatives can be prepared by this method.

N. H. M.

Has Creatinine Basic Properties? By E. SALKOWSKI (*Zeit. physiol. Chem.*, 12, 211—215).—Creatinine has not the strongly alkaline reaction commonly ascribed to it, but that reaction is dependent on impurities mixed with it, namely, certain constituents of the ash, especially the barium carbonate used in its preparation. The minimal alkaline reaction of the purest possible preparation is also due to a similar slight admixture with ash. 0.113 gram of pure creatinine was dissolved in water, and it was found that a single drop of $\frac{1}{4}$ normal sulphuric acid neutralised the alkaline reaction, and two drops gave an acid reaction; whereas the quantity necessary to neutralise such an amount, had a compound with the acid been formed, would have been 4 c.c. The question was then re-investigated, whether creatinine is able to displace ammonia from ammonium salts. The salt employed was ammonium chloride. In the first place a certain amount of the ammonium chloride solution was distilled, and the ammonia in the distillate estimated colorimetrically by Nessler's reagent. The same amount of the salt solution was then distilled with a known weight of creatinine; and the amount of ammonia in the distillate was found to be much increased, five times as much ammonia being evolved. Control experiments showed that this could not have been yielded by the creatinine itself, nor by the action of the ash of the creatinine on the ammonium chloride; therefore creatinine itself has the action in question. Other nitrogenous substances which form salts, especially the amido-acids, might be expected to act in like manner, but leucine

was not found to do so. It is also possible on the other hand that excess of ammonia will decompose creatinine-zinc chloride. On heating an aqueous solution of creatinine-zinc chloride with excess of ammonia, a deposit of zinc oxide is formed; if the boiling is continued until there is no more deposit, the solution is found to be neutral, contains ammonium chloride and creatinine, but only traces of zinc. If it is evaporated to dryness, the residue taken up with alcohol, the alcoholic extract evaporated to dryness, and the residue taken up with water, and zinc chloride solution added, creatinine zinc chloride is again formed.

W. D. H.

Creatinine. By G. S. JOHNSON (*Proc. Roy. Soc.*, **42**, 365—370).— $\frac{1}{20}$ th of its volume of a saturated solution of sodium acetate is added to fresh urine, and then $\frac{1}{4}$ th of its volume of saturated mercuric chloride. The precipitate of mercuric urate first produced is filtered off, and the liquid left for 48 hours, when a granular precipitate falls, having the composition $4(C_4H_7N_3O, HCl, HgO), 3HgCl_2$. It is soluble in hydrochloric acid, insoluble in acetic acid. When moistened with aqueous potash it blackens, and much "compound ammonia" is evolved. By decomposition with hydrogen sulphide, the hydrochloride is obtained, and from this by decomposition by lead hydroxide, the free base, $C_4H_7N_3O$, crystallising in square plates with bevelled edges; an efflorescent hydrate, $C_4H_7N_3O, 2H_2O$, can also be obtained, crystallising in long prisms. The aqueous solution of the base is strongly alkaline, has a bitter taste, and gives crystalline precipitates with zinc and mercuric chlorides or picric acid, but none with silver nitrate. It reduces cupric oxide in the proportion of 12 : 10. The average weight passed in 24 hours is 1.7 to 2.1 gram = 1.5 to 1.75 gram glucose. The platinochloride crystallises in orange-coloured prisms, and has the composition



A comparative table of various creatinines is given.

H. K. T.

Formula of Morphine. By D. B. DOTT and R. STOCKMAN (*Pharm. J. Trans.* [3], **18**, 708).—After elaborate investigation, Wright decided that the formula of morphine must be at least double the empirical one, that is, it should be $C_{34}H_{38}N_2O_6$; but the authors have failed to obtain confirmation of Wright's views, either from their own experiments or from a repetition of his. They conclude that the formula $C_{17}H_{19}NO_3$ ought to be retained, as it is consistent with all that is known of the alkaloid, and they suggest that probably the substances with which Wright operated were mixtures.

R. R.

Morphine Hydrate. By D. B. DOTT (*Pharm. J. Trans.* [3], **18**, 701).—The author finds that, contrary to the statements of all the authorities, a temperature below 100° suffices to deprive morphine of all its water of crystallisation. He infers from his results that the hydrate has the formula $8C_{17}H_{19}NO_3 + 9H_2O$, and not $C_{17}H_{19}NO_3 + H_2O$ as usually stated.

R. R.

Derivatives of Cinchonine. By E. JUNGLEISCH and E. LÉGER (*Compt. rend.*, **106**, 68—71).—The isomerides of cinchonine previously described (this vol., p. 380) are separated by precipitation with soda, washing the precipitate, and treating it with ether.

The ethereal solution is heated to expel ether, and neutralised with hydrochloric acid. After some days, cinchonigine hydrochloride crystallises out, and a fresh crop of crystals can be obtained by concentrating the mother-liquor. If the mother-liquor is then precipitated with soda, the precipitate extracted with ether, the ether expelled, and excess of colourless hydriodic acid added, a yellow, crystalline precipitate of cinchoniline dihydriodide is obtained. After separation of these two alkaloids, the liquid contains a small quantity of a base which has yet to be examined.

The portion of the original precipitate insoluble in ether, is dissolved in strong, boiling alcohol, distilled until crystals separate in the hot liquid, and mixed with an equal volume of water. After standing overnight, the precipitate is dissolved in water containing succinic acid, and the solution concentrated, when it deposits needles of cinchonibine succinate, a further quantity of which is obtained by again concentrating. The mother-liquor is precipitated with soda, and the precipitate dissolved in colourless hydriodic acid to form a neutral solution, which after some time deposits crystals of cinchonifine hydriodide.

The dilute alcoholic solution is distilled, and the aqueous residue neutralised with hydrochloric acid, and filtered whilst boiling. The filtrate deposits crystals of α -hydroxycinchonine hydrochloride. When no more crystals of this compound can be obtained from the concentrated mother-liquor, it is neutralised with soda, mixed with acetone, and the precipitate of β -hydroxycinchonine washed with acetone.

C. H. B.

Action of Oxalic Acid on Cinchonine in Presence of Sulphuric Acid. By CAVENTOU and C. GIRARD (*Compt. rend.*, **106**, 71—73).—Cinchonine when heated at 125—130° with oxalic acid and monohydrated sulphuric acid for several days is partly converted into two bases, one of which is soluble in both ether and benzene, whilst the other is soluble in ether but insoluble in benzene. The first has the same composition as cinchonine, but forms large crystals which retain benzene unless heated at 100°; it dissolves in acetone, chloroform, and methyl, ethyl, and amyl alcohols. It melts at 125°, and its laevorotatory power in a 1 per cent. alcoholic solution is $[\alpha]_D - 58^\circ 3'$. With potash, it yields quinoline and pyridine-derivatives. The hydrochloride is soluble in water, and crystallises readily, its rotatory power is $[\alpha]_D = -68^\circ 28'$. The platinochloride is orange-yellow, and dissolves in hot water; the sulphate crystallises well, but is very soluble; the chromate is orange, and somewhat soluble in water, differing in this respect from cinchonine chromate. The physiological action of this base is similar to that of cinchonine, but more energetic.

The base insoluble in benzene and the other products soluble in ether have not yet been examined.

C. H. B.

Hygrine. By R. STOCKMAN (*Pharm. J. Trans.* [3], **18**, 701).—Hygrine exists in only a very minute amount in dried coca leaves, probably because it is volatilised in the process of desiccation, but from an alcoholic extract of the fresh leaves, the author obtained it in relatively larger quantity, as a brown oily liquid, with a characteristic smell and burning taste, and an alkaloidal reaction. It is an extremely irritating substance, and a drop placed on the tongue causes a burning sensation. When a drop mixed with water is injected under the skin of a frog, the animal dies after a time, and all the muscles, bowels, and serous membranes are found studded with minute hæmorrhages. Hence hygrine must be carefully eliminated from all therapeutic preparations of cocaine. R. R.

Cholic Acid. By F. MYLIUS (*Zeit. physiol. Chem.*, **12**, 262—266; compare Abstr., 1887, 606, 982).—The author repeats in detail his method of preparing cholic acid; it crystallises from absolute alcohol in tetrahedra of the composition $C_{24}H_{40}O_5, C_2H_6O$. Much cholic acid remains in solution in the alcohol; he considers it possible, although he has not worked definitely at the subject, that a form of cholic acid exists which does not yield a crystalline compound with alcohol. The formula $C_{24}H_{40}O_5$ for cholic acid is that originally ascribed to it by Strecker. He criticises the work of Latschinoff on this subject, who has recently (this vol., p. 303) given $C_{25}H_{42}O_5$ as the formula for cholic acid. He considers that the aniline and toluidine cholates are unsuitable compounds on the analysis of which to found a formula, and also considers it improbable that such compounds as $C_{25}H_{42}O_5 + \frac{1}{8}H_2O + \frac{7}{8}C_2H_6O$, or $C_{25}H_{42}O_5 + \frac{1}{8}H_2O + \frac{7}{8}C_6H_6O$ exist.

W. D. H.

Colour Reactions of Proteïds. By E. SALKOWSKI (*Zeit. physiol. Chem.*, **12**, 215—222).—A part of the proteïd molecule belongs to the aromatic group of compounds, and it is on the presence of aromatic radicles in proteïds that the well-known colour reactions given by those substances depend. By the putrefaction of proteïds, aromatic substances are formed, which fall into three groups: (1) the phenol-group, including tyrosine, aromatic hydroxy-acids, phenol, and cresol; (2) the phenyl-group, which contains phenylacetic and phenylpropionic acid; and (3) the indole-group, of which indole, scatole, and scatolecarboxylic acid are the most important members. Whether all three groups exist preformed in the proteïd molecule, or whether that molecule contains only one aromatic group, and the others are easily derived from this one on decomposition (Maly), matters little in a solution of the question investigated, namely, on which of the groups do the colour reactions depend. These colour reactions were tried with each of the substances enumerated, and the following were the results obtained:—

1. *Millon's Reaction.*—This does not occur in presence of sodium chloride. Kühne considers that the reaction is due to tyrosine; O. Nasse that it is dependent on those benzene-derivatives in which only one atom of hydrogen is displaced by hydroxyl. In this research, it was found to be given only by substances enumerated under the first group. The precaution must be taken to prepare the reagent as

originally described. Gelatin also gives the reaction faintly; the purest gelatin yields traces of phenol (Weidel and Ciamician, *Ber.*, **14**, 1009).

2. *The xanthoproteic reaction* depends without doubt on the formation of nitro-derivatives. The trinitro-albumin and oxytrinitro-albumin of Low (this Journal, 1872, 1028) are very doubtful chemical units. Nencki and Sieber (*Abstr.*, 1885, 826) have obtained para-nitrobenzoic acid by the action of fuming nitric acid on dry albumin, but as this acid is colourless, it cannot be that which gives the yellow colour. The substances enumerated in the first group give the reaction strongly; those in the third group give it well, but not so well as those in the first group; indole gives it feebly, except when fuming nitric acid is used; and the substances in the second group do not give it at all, or exceedingly faintly. The xanthoproteic reaction can be used to determine peptone or perhaps albumin quantitatively in an approximate manner. It is much better than the violet or pink tint caused by copper sulphate and potassium hydroxide, as proposed by Schmidt-Mülheim, for three reasons: (1) gelatin and gelatin peptone do not give the xanthoproteic reaction; (2) the shade as well as the intensity of the colour varies greatly in the copper sulphate test; and (3) the colour of the original solution does not interfere with this test, except in very exceptional cases.

3. *The Adamkiewicz Reaction.*—This test is given by all proteïds, including albumoses and peptones, but not by gelatin or its peptones. It is not, however, a certain test, and in the case of albumoses and peptones is given only with concentrated solutions. It is given only by the aromatic substances of the third (indole) group, and especially by scatolecarboxylic acid. The addition of a minimum quantity of potassium nitrite intensifies the colour, as it does also in solution of proteïds; a further addition of that salt turns the purple colour to red.

4. *The colour reaction with strong hydrochloric acid* (Liebermann, *Abstr.*, 1887, 1150) is not given by any of the aromatic substances enumerated.

W. D. H.

Albumoses and Peptones. By R. NEUMEISTER (*Zeit. Biol.*, **24**, 267—271).—In a former article (*Abstr.*, 1887, 285), the author has shown that deuto-albumoses are more allied to peptones than the primary albumoses (proto- and hetero-albumose), not only aetiologically but also in their chemical reactions. Deuto-albumose is for instance not precipitated, as are the primary albumoses, by saturation with sodium chloride, nitric acid in the absence of salt, nor by cupric sulphate. To this list, must now be added saturation with ammonium sulphate for one variety of deuto-albumose; the deuto-albumose which is formed from hetero-albumose, and also that formed from anti-albumid, is completely precipitated by saturation with ammonium sulphate; but the form of deuto-albumose (probably hemi-deuto-albumose) which is formed from proto-albumose, is to a certain extent soluble in saturated solutions of ammonium sulphate, even in the presence of acetic or sulphuric acid.

The different albumoses may be prepared in a pure state as follows:

—"Witte's peptone" is completely dissolved by prolonged digestion with 3 per cent. hydrochloric acid at 40°; the solution is then neutralised, and saturated with sodium chloride; the precipitate which contains the two primary albumoses is redissolved, and hetero-albumose precipitated by dialysing out the salt from the solution. The proto-albumose remains in solution with a certain amount of deuto-albumose, from which it is separated by saturating the boiling solution with ammonium sulphate; the precipitate of proto-albumose is collected, redissolved, and the saturation repeated until the filtrate does not give the biuret reaction. Its solution is then dialysed, concentrated, alcohol added, and the resulting precipitate washed with ether and dried in a current of dry air. The hetero-albumose is purified by prolonged washing with cold water, in which it is, however, not so insoluble as has been hitherto supposed (this solubility increases at a temperature of 40°); it is then redissolved, precipitated by ammonium sulphate, and the rest of the process is the same as with proto-albumose.

The deuto-albumoses are present in the filtrate after the precipitation of the primary albumoses; they are separated from the peptone by means of acetic acid saturated with ammonium sulphate; the precipitate of the deuto-albumoses is dissolved in water, boiled, and saturated with ammonium sulphate; a certain amount of the hemi-deuto-albumose remains in solution; the precipitated deuto-albumose is redissolved and the operation repeated, until a precipitate is obtained which is wholly soluble in water, and on saturating which with ammonium sulphate no proteid is left in solution; this deuto-albumose is then freed from salt and purified as in the other cases. The hemi-deuto-albumose is obtained by concentrating the filtrates.

W. D. H.

Nuclein from Yeast: Artificial Preparation of Nuclein from Albumin and Metaphosphoric Acid. By L. LIEBERMANN (*Ber.*, 21, 598—600).—The results here detailed seem to show conclusively that the nucleins are compounds of albumins with metaphosphoric acid. When yeast nuclein is extracted with cold dilute nitric acid, metaphosphoric acid goes into solution, whilst the residue no longer gives the characteristic reactions of nuclein. On the other hand, the precipitate obtained by adding metaphosphoric acid to a solution of egg albumin, cannot be distinguished from the nucleins either in composition or reactions. It is strange that this precipitate, so well known in testing for albumin, should never have been investigated.

A. J. G.

Resistance of Hæmoglobin towards different Decomposing Agents. By F. KRÜGER (*Zeit. Biol.*, 24, 318—335).—The hæmoglobin of different animals differs in solubility, in the readiness with which it crystallises, and in crystalline form. Körber (*Inaug. Dissert.*, Dorpat, 1866) stated that hæmoglobin differs also in the readiness with which it is decomposed by such reagents as acetic acid and sodium hydroxide. He published tables of numerous comparative observations on the resistance to decomposition of the hæmoglobin of different animals. He found that the absorption-bands of hæmoglobin of the dog and man disappeared within a minute after the addition

of these reagents, whereas in that of herbivorous animals the bands did not completely disappear for several hours when similarly treated. He obtained solutions of hæmoglobin of approximately equal strength by diluting the defibrinated blood with water, till it assumed a standard tint. Körber's results have been considerably criticised (for instance, by Preyer, *Die Blutkrystalle*, Jena, 1871, p. 61), as his experiments were not made with pure hæmoglobin, but in the presence of the other constituents of the blood.

The present research was undertaken with a view of testing the same matter similarly, but accompanied by control experiments with pure hæmoglobin; the hæmoglobin was estimated by means of Hüfner's spectrophotometer (Abstr., 1887, 1126). The blood crystals were dissolved in a 0·1 per cent. solution of sodium hydroxide instead of distilled water. The hæmoglobin of the dog and horse only were examined as examples of the pigment, in which Körber states the difference in their resistance to decomposition is very marked. The time between the addition of the reagent and the disappearance of the absorption-band was noted. The following gives in tabular form an example of the kind of experiment performed and results obtained:—

Time in Minutes in which a 10 per cent. Solution of Acetic Acid and Sodium Hydroxide respectively caused the Decomposition of 0·05 gram of Hæmoglobin in Solution.

	Amount of acetic acid added in c.c.	Time.		Amount of soda added in c.c.	Time.	
		Dog.	Horse.		Dog.	Horse.
Blood and water ...	0·5	64	350	0·25	78	380
„ ...	1·0	24	219	0·50	10	104
„ ...	1·5	10	111	1·00	1·5	54
Hæmoglobin after one crystallisation dissolved in water	0·5	65	350	0·25	77	310
	1·0	25	189	0·50	11	104
	1·5	12	106	1·00	1·25	44
Hæmoglobin after two crystallisations dissolved in water	0·5	65	350	0·25	79	310
	1·0	24	189	0·50	11	104
	1·5	12	106	1·00	1	44

That it is the hæmoglobin itself and not any other constituent of the blood that causes this difference was shown by taking the blood corpuscles of one animal, and by the use of a centrifugal separator ridding them of serum, and then adding the serum of the other animal to the corpuscles. The hæmoglobin under these circumstances retained its characteristic resistance to the reagents used.

The conclusions finally drawn from such experiments are:—(1.) That Körber's statement regarding the great difference in the power with which the hæmoglobin of these two animals resists the decomposing

action of acetic acid and sodium hydroxide is perfectly correct, and that moreover Körber's method is one which leads to correct results. (2.) That this difference is due to a difference in the chemical composition of the hæmoglobin itself. (3.) The difference between the resistance of the two forms of hæmoglobin examined increases with the quantity of the reagent used. (4.) Within the limits of the quantities used in experiments, such as the one given here in detail, sodium hydroxide is the more powerful reagent of the two.

W. D. H.

Activity of Reduction of Oxyhæmoglobin. By A. HENOCQUE (*Compt. rend.*, **106**, 146—147).—An account of the variations in the activity of reduction of oxyhæmoglobin in various diseases under the influence of various drugs.

C. H. B.

Physiological Chemistry.

Rapid Absorption of Carbonic Anhydride from Expired Air.

By A. D'ARSONVAL (*Compt. rend. Soc. Biol.*, **4**, 750—751, and 751—753).—The difficulty of wholly absorbing all the carbonic anhydride from expired air is completely overcome by submitting the air to a fine spray of the potash solution. This is accomplished with an apparatus which is essentially a spray-producer. The spray is produced by suction, and the expired air drawn through a tube with which the spray-producer is concentric. An apparatus is also described for permitting a person to breathe in a limited atmosphere of constant composition, and for registering the absorption of oxygen, and the disengagement of carbonic anhydride. J. P. L.

Absorption of Carbonic Anhydride, and Graphic Record of the Carbonic Anhydride Expired. By M. HANRIOT and C. RICHET (*Compt. rend. Soc. Biol.*, **4**, 753—754).—Complete absorption of the carbonic anhydride is effected by passing the air through a burette $1\frac{1}{2}$ metres long filled with broken glass over which potash flows. A method is explained for graphically recording the oxygen absorbed and carbonic anhydride exhaled. J. P. L.

Formation of Ammonia in the Pancreatic Digestion of Fibrin. By E. STADELMANN (*Zeit. Biol.*, **24**, 261—266).—Hirschler (Abstr., 1886, 726) has stated that small quantities of ammonia are formed during the pancreatic digestion of fibrin; but as in his experiments the fibrin that was used had not been previously boiled, and the mixtures were not thymolised or otherwise rendered antiseptic, his results are not considered satisfactory. In the present research, such antiseptic measures were adopted, and putrefaction entirely prevented. Some of the mixture before digestion was distilled with sodium carbonate, and the distillate titrated with sulphuric acid; a small amount of ammonia was present, but this was not increased even after digestion had gone on for 10 days.

The conclusion was therefore drawn, either that no ammonia is formed, or that if it is, it is combined in such a manner, that distilling with sodium carbonate does not drive it off.

To solve this question, the following method was adopted; the digestive mixture was filtered; the filtrate distilled, and the distillate received in hydrochloric acid; to the residue, a few drops of acetic acid were added, then excess of *magnesia usta*, and it was again distilled, and the distillate collected as before. Both filtrates were evaporated and treated with platinic chloride; the resulting precipitates washed with alcohol and ether, ignited, and the ammonia calculated from the weight of the platinum residue.

By this method, it was found that Hirschler's statement was fully confirmed as to the occurrence of ammonia; although whether it is present as an ammonium salt, or in some hitherto unknown organic compound, there is not sufficient evidence to say. W. D. H.

Influence of Phenylacetic Acid on Proteid Metabolism. By E. SALKOWSKI and A. KOTOFF (*Zeit. physiol. Chem.*, **12**, 222—226).—Researches were made on dogs:—the animal first received 50 c.c. of milk only daily for a few days, and then for some days with the addition of 2 grams of sodium phenylacetate dissolved in water. The animals generally died in three or four days after this compound was given.

Taking an average of the five series of researches, the following numbers were obtained relating to the amount of nitrogen and sulphuric acid passed in the 24 hours:—

	Daily average.		
	N.	Total SO ₃ .	Combined SO ₃ .
Phenylacetic acid not given ..	1.254	0.120	0.038
" " given	1.921	0.256	0.028

The decomposition of proteid is thus increased, though why the amount of sulphuric acid is increased in such greater proportion than the nitrogen it is at present impossible to say. The decrease in the combined sulphuric acid (ethereal hydrogen sulphates) is doubtless due to the antiseptic action of the compound administered. As was pointed by Müller (*Zeits. f. Klin. Med.*, **12**, 19), the absolute quantity of ethereal hydrogen sulphates in the urine is a much more correct measure of the amount of putrefaction going on in the intestine, than the relation between those sulphates, and the normal sulphates of the urine. W. D. H.

The Output of Chlorides in its Relation to Metabolism. By A. KAST (*Zeit. physiol. Chem.*, **12**, 267—284).—The automatic regulation of the discharge of chlorides, according to Forster (*Zeit. Biol.*, **9**, 297), depends on the decomposition of proteids; the "circulating proteids" (Voit) which are in combination with much salt being decomposed before the "tissue proteids," which are comparatively poor in the amount of salt associated with them. This view is supported by Röhmman (*Zeit. klin. Med.*, **1**), among others, who points out that the clinical facts observed in fever, especially in pneumonia, with regard to the diminution of chlorides in the urine, fully bear it out.

As a result of the present researches, this theory must, however, be modified. The chief observations made are as follows. Chloroform poisoning is followed by an increase of the amount of chlorine in the urine (see Abstr., 1887, 612), and this is accompanied by the presence of abundance of biliary colouring matter in that secretion. In chronic chloroform poisoning, the total metabolism that ensues is diminished, and the animal gains weight.

Starvation in animals previously deprived of chlorides produces an increase in the chlorides excreted (Forster).

Removal of blood from a dog produced a considerable diminution of the chlorides excreted for the four days following the venesection. The diet of the animal in this and similar experiments was constant. This coincides with what is known clinically with regard to the diminution of chlorides in the urine after hæmorrhages in man. The influence of carbonic oxide was next investigated; in normal animals, and in those who have been previously saturated with a large excess of chlorides in the diet, carbonic oxide poisoning was followed by lessening of the chlorides excreted; whilst in those which had been previously deprived of chlorides, it produced an increase of the total chlorides of the urine. The minimum of chlorides in the first case was reached a few days after the poisoning; and the less chlorides in the urine the more strongly did that secretion reduce Fehling's solution. If Forster's explanation of the excretion of chlorides is correct, it must also be supposed that under certain conditions the reverse is also true; namely, that the "organ-albumin" contains more salt than the "circulating-albumin." Phosphorus poisoning was found to produce abundant destruction of proteid with rise of the daily nitrogen in the urine, but a diminished quantity of chlorides.

In view of the appearance of biliary colouring matter in the urine of chloroform narcosis, it was thought possible that some relation might exist between the destruction of red corpuscles and the amount of chlorides in the urine. Bunge (*Zeit. Biol.*, 12, 191) has shown that sodium chloride is a constant constituent of red blood corpuscles. With a view to testing this opinion, pyrogallol was administered to dogs; this produced blood-tinted urine, albuminuria, and greatly increased chlorides in the urine; this corresponds with the destructive influence of this drug on the red corpuscles. The administration of toluylenediamine produces similar result, but is more trustworthy as it produces no albuminuria. Albuminuria in Bright's disease is, however, not necessarily associated with an increased discharge of chlorides.

The conclusion is therefore drawn that there are two distinct factors concerned in regulating or altering the amount of chlorides in the urine; first, proteid metabolism, to which the output of chlorides is usually in the inverse ratio, and secondly, disintegration of red blood corpuscles, to which it stands in a direct ratio. That when, moreover, the two processes occur simultaneously, the final result depends on which of them it is which preponderates. W. D. H.

Fate of Pyridine in the Organism. By O. DE CONINCK (*Compt. rend. Soc. Biol.*, 4, 755—756).—His (*Archiv Expt. Path. Pharm.*, 22,

253) states that pyridine acetate when given by the stomach to dogs does not pass through unchanged, but appears in the urine as picoline, C_6H_7N , of which he prepared the platinochloride and aurochloride.

This is contrary to the author's experience. In a series of experiments which he made in conjunction with Bochefontaine in 1884 with the hydrochloride, pyridine was always secreted unchanged, at least the greater part, in urine, saliva, and breath. The discrepancy might possibly be explained by assuming the addition of a CH_3 -group to the pyridine molecule as a result of the decomposition of the acetate in the body. J. P. L.

Nutritive Value of Vegetable Proteïds compared with that of Animal Proteïds. By J. RUTGERS (*Zeit. Biol.*, 24, 351—381).—These experiments were carried out in human beings. Tables are given of the diets employed, at one time containing animal food, at another being an almost exclusively vegetable diet. In all the constituents of the food, the nitrogen, fat, extractives free from nitrogen, sugar, and alcohol were estimated; and the urine and fæces were daily examined, the nitrogen especially being estimated; simultaneous observations were made on the body-weight. The conclusions that are drawn from the results obtained may be thus summarised:—

Vegetable proteïds containing an equal amount of nitrogen can be substituted for the animal proteïds which were used without the nitrogenous balance of the body being disturbed. Beans and peas load the intestinal tract very much, both in respect of their solid constituents and of the gases formed from them; meat and rice have not this disadvantage. This and other contra-indications of a similar nature would render an exclusively vegetable diet undesirable. The acidity of the stomach and also that of the urine is much smaller when the diet is exclusively vegetable than when a mixed diet is taken.

Milk, if it is not taken as the exclusive means of nutrition, is in adults also very completely digested. The questions of the difference in cost of the two diets was found to be regulated only by the cost of heating the oven.

The mean values given by Moleschott as the daily amount of nutriment necessary were not found to be too low for the climate in which the experiments were carried out (Holland). Kjeldahl's method of estimating nitrogen was found to be the best not only for urine and milk, but for fæces also. The method of Pflüger and Bohland for estimating quickly and approximately the nitrogen in human urine yields, especially when the urine is rich in urea, better results than the improved Liebig's method. W. D. H.

Cellulose in the Nutrition of Herbivorous Animals. By W. v. KNIERIEM (*Zeit. Biol.*, 24, 293—305).—In a paper by Weiske and others (Abstr., 1886, 728), the conclusion was drawn that cellulose does not economise the decomposition of proteïd, which was precisely the opposite conclusion to that which v. Knieriem, from his former experiments, arrived at (Abstr., 1885, 916). The present paper takes up the subject again, the author reiterating his former views, and criticising the methods, results, and conclusions of Weiske.

W. D. H.

Physiological Action of Albumoses and Peptones. By R. NEUMEISTER (*Zeit. Biol.*, **24**, 272—292).—The fate of the products of digestion of proteids has been the subject of researches by Maly, by Plósz and Gyergyai, by Adamkiewicz and others. Schmidt-Mülheim (*du Bois Reymond's Archiv*, 1880, 33) thought that the products of digestion were absorbed as such, and in the blood became quickly transformed into albumin. An injection of so-called peptone (really albumoses and peptones) into the circulation, vanished as such in a few minutes, and was not observed in the urine; this did not occur when "peptone" was mixed with shed blood. After abundance of proteid food, small quantities of "peptone" were found in the circulating blood.

Hofmeister (*Zeit. physiol. Chem.*, 1881, 127) found, on the other hand, that injection of "peptone" into the circulating blood was followed by its rapid disappearance from the blood and appearance in the urine. But it as quickly disappears if the quantity injected is sufficient to so lower the blood pressure as to suppress the secretion of urine altogether. He considers that it collects in certain organs, liver, kidneys, &c., under these circumstances. He was able sometimes to discover peptone in the circulating blood during digestion, but supposes that ordinarily it enters into combination with the white blood corpuscles and so escapes detection.

In the present paper it is shown that the methods used by the investigators just quoted, for the identification of peptones is untrustworthy; the method of heating, after acidifying to remove other proteids, and then calling the still soluble proteid, "peptone," if it gives the biuret action, is a method which in reality leads to the formation of small quantities of primary albumose, as heating with acid is one means of obtaining these hydration products of proteids. Milk is taken as an example of a substance in which such artificial products have been described under the name of peptone, hemialbumose, lactoprotein, &c., by various observers as normal constituents of that secretion. Pus also, which is generally said to contain peptone, was found by improved methods to contain none. These improved methods are as follows:—First, the liquid is precipitated by alcohol; the proteid precipitate is allowed to remain under absolute alcohol for some weeks, by which time all proteids but albumoses and peptones are rendered insoluble; the albumoses and peptones can then be removed by extracting the precipitate with water, and identified in solution by their characteristic tests. Peptone and one form of deuterio-albumose could be identified in the blood by first receiving it into a solution of ammonium sulphate to prevent coagulation; then dissolving the corpuscles by adding ether; removing the ether; and saturating with ammonium sulphate and filtering; the filtrate would contain deuterio-albumose and peptone if present. The lymph, urine, and other fluids can be similarly investigated. It was found that peptones or albumoses never (or only in the merest traces) occurred in the blood or lymph, even when the most energetic digestion of proteids was going on in the alimentary canal. It was found that injection of albumoses or peptones or both into the circulation was followed by their rapid and complete disappearance therefrom and appearance in the urine within 10 minutes,

both in the dog and rabbit; but they also disappear when the ureters are tied. There was no rise of temperature as described by Ott and Collmar (*Med. News*, 1887, February 19). In the dog, it was found that the albumoses, after the injection, underwent hydration before they appeared in the urine; the primary albumoses appearing mostly as deuto-albumoses, and the deuto-albumoses as peptones. This occurred in the urine when it was acid, neutral, or alkaline, and could not be due to digestion by the pepsin contained in the urine, when the latter remained in the bladder. Albumoses even when mixed with acid urine underwent no such change; the large percentage of salts present, and the fact that the acidity is not due to free acid would prevent this. Contact of the albumoses with freshly-drawn blood, or with fresh organs such as liver or kidney, also caused no change in them. The view is advanced that they are digested by the pepsin secreted by the kidneys in the urinary tubules where there is momentarily a formation of free acid. In the rabbit, no such change occurs; the urine contains no pepsin in this animal, and the albumoses injected into the circulation are secreted as such.

W. D. H.

Physiological Action of the Products of Incomplete Combustion of Illuminating Gas. By N. GRÉHANT (*Compt. rend. Soc. Biol.*, 4, 779—780).—To determine the action of the products of the incomplete combustion of illuminating gas, a dog was placed for two hours in a chamber of 12 cubic metres' capacity, in which a Bunsen burner burning at the bottom was also placed.

A comparison of the gases of the blood taken from the carotid artery, before and after the experiment, showed that the oxygen of the original blood was almost wholly displaced by carbonic oxide.

J. P. L.

Action of Ethylene Chloride on the Cornea. By R. DUBOIS and P. ROUX (*Compt. rend. Soc. Biol.*, 4, 584—585).—With the object of establishing some relation between chemical constitution and physiological action, the authors have commenced the study of the chlorine-derivatives of ethane, many of which possess anæsthetic properties. The first compound they have experimented with is ethylene chloride, which is found to have a remarkable action on the cornea.

If a dog is anæsthetised for one hour by inhalation of ethylene chloride, or if the compound is injected subcutaneously, both corneas, especially if the anæsthetising is repeated after the lapse of 24 to 36 hours, become opalescent and of a bluish-white tint, which give to the animal a strange appearance, the curves of the cornea become especially exaggerated in the vertical meridian, where it is easy to show astigmatism. The bluish-white tint and the abnormal prominence of the cornea recall a double symmetrical opaque anterior staphyloma. This experimental lesion is permanent.

Operation for glaucoma was successfully performed on one of the animals; the eye operated on remaining transparent whilst the other became opaque; the cornea is the only part of the eye which appears to be affected.

J. P. L.

Pigments of Melanotic Sarcomata. By K. A. H. MÖRNER (*Zeit. physiol. Chem.*, **12**, 229—240).—Nencki (*Arch. exp. Pathol. Pharm.*, **24**, 27) has criticised the previous publication of the author on this subject (*Abstr.*, 1887, 168). The present reply to this criticism points out that in the previous paper it is distinctly stated that the analyses given refer to two different pigments, one soluble and the other insoluble in acetic acid, and not to one only as Nencki has supposed.

The author also shows that in Nencki's analyses very great differences occur, and that in some cases the percentages are incorrectly calculated.

W. D. H.

Therapeutic Substitutes for Chrysarobin. By C. LIEBERMANN (*Ber.*, **21**, 447—452).—The analogy of the leuco-derivatives of the anthraquinone-dyes (this vol., p. 492) to chrysarobin, the active principle of Goa powder, suggested that the therapeutic action would be similar. This has proved to be the case, as it is found that they will also cure those skin diseases for which chrysarobin is at present employed. They are, therefore, being made on the commercial scale under the name of "*anthrarobins*;" the term *anthrarobin* being more particularly applied to the reduction product from commercial alizarin. The reduction on the large scale is best effected by means of zinc-dust and ammonia. The activity of anthrarobin is reported to be about equal to that of chrysarobin, but more intense than that of pyrogallol; anthrarobin has the advantage that it does not produce inflammation of the skin.

The author is inclined to attribute the therapeutical activity of both chrysarobin and the anthrarobins to their great affinity for oxygen.

A. J. G.

Urea and Total Nitrogen in Human Urine. By W. CAMERER (*Zeit. Biol.*, **24**, 306—317).—Of every 100 grams of nitrogen obtained from urine, 90 are on the average derived from urea and ammonia; and the remaining 10 from other nitrogenous constituents called extractives. The object of this research was to determine the relation between these two sources of nitrogen under certain conditions. The total nitrogen was estimated by the Varrentrapp-Will method, and the nitrogen from urea by Hüfner's hypobromite method; the small amount of nitrogen yielded by uric acid and creatinine on treating urine with hypobromite was not taken into account, so that the percentage differences in the tables given are a little too small.

For 15 days, the total urine in each 24 hours was collected, its quantity measured, its specific gravity taken, and the nitrogen in it estimated by the two methods. The average of the results of the 15 days, the average of those of the seven of the 15 days when the total percentage of nitrogen was above the average, and the average of those of the remaining eight days when it was below the average, are given in the following table:—

	Average results per diem		
	For the fifteen days.	For the seven days in which the average was exceeded.	For the eight days in which the average was not reached.
Specific gravity	1·016	1·018	1·014
Quantity in c.c.	1840	1488	2147
Total nitrogen	16·06	15·77	16·31
Nitrogen from urea	14·15	14·13	14·17
Total nitrogen.	0·873	1·06	0·76
Nitrogen from urea } per cent. }	0·769	0·95	0·66
Difference	11·9	10·4	13·1

From this it appears that the increase of the total quantity of urine excreted is accompanied by diminished specific gravity, and that the excretion of extractives is increased both absolutely and proportionally to the total of nitrogenous substances in the urine; the total quantity of nitrogen from extractives in the group of seven days averaging 1·64 gram, and in the other group 2·14. A second series of observations was made to determine the influence of proteid food on the output of both sources of nitrogen. The experiment was carried out on four persons, each of whom partook of one meat meal in the 24 hours, and whose urine was collected at intervals of three hours. Details similar to those enumerated in the previous experiments are tabulated, and the general results are the following:—The increase in both kinds of nitrogen commences almost immediately after the digestion of the proteid food; the nitrogen derived from urea reaches its maximum in from 7 to 10 hours, whilst that derived from the extractives is greatest in the four first hours after the commencement of the meal. The percentage difference is greatest during the first three hours and smallest 12 hours after the meal. The quantity of urine is smallest during the first four hours, and greatest from 7 to 10 hours after the meal; the most concentrated urine is thus accompanied by the secretion of the maximum of extractives, which is the opposite to the general result obtained from the first series of experiments.

From the large number of experiments performed, it is found that on the average for every 100 grams of nitrogen found by Hüfner's method, 13·6 must be added to obtain the total nitrogen; and this method of calculating the total nitrogen gives very good practical results.

W. D. H.

Cystin in Normal Urine. By E. GOLDMANN and E. BAUMANN (*Zeit. physiol. Chem.*, 12, 254—261).—Stadthagen (Abstr., 1885, 830) has stated that normal urine contains no cystin, or only minimal quantities of that substance. In 12 experiments, the average amount of sulphur from cystin or allied substances was only 0·0003 gram per litre of urine.

It was thought necessary to repeat these observations, because investigations on the properties of pure cystin showed that Stadthagen's method was not calculated to yield accurate results.

If a few drops of benzoic chloride is added to a solution of pure cystin in sodium hydroxide, a voluminous precipitate of shining plates of the sodium salt of benzoylcystin, $C_6H_{10}N_2S_2O_4Bz_2$, is produced. This salt is soluble in hot, less soluble in cold water, and quite insoluble when excess of sodium hydroxide is present. By adding acid to this, benzoylcystin itself is obtained. It is a strong acid, insoluble in water, slightly soluble in pure ether, more so in a mixture of alcohol and ether, and still more so in alcohol. It crystallises in slender needles, melts at $156-158^\circ$, and is decomposed into benzoic acid and cystin by boiling with strong acids. By boiling with alkalis, it yields up its sulphur like cystin.

The circumstance that this compound is easily separated from watery fluids by means of ether, renders it easy to obtain cystin from the urine when it is present there. In some preliminary experiments known weights of benzoylcystin were mixed with urine, extracted therefrom by ether; the ethereal solution was evaporated to dryness, the residue taken up with sodium hydroxide, and the sulphur weighed as lead sulphide. The lead sulphide obtained, however, only corresponded to about two-thirds of the cystin used. On treating normal urine in this way, a precipitate of lead sulphide was always obtained, and the amount of sulphur was always greater than in Stadthagen's experiments, but as the cystin is not all decomposed, no exact quantitative statements can be made. The statement commonly made that cystin gives up its sulphur easily and completely on heating with alkalis is incorrect; after many hours' boiling, the cystin still retains a large percentage of sulphur, and this percentage is still greater in the presence of the other constituents of urine. It can, therefore, be said that cystin or a substance like cystin always occurs in urine, but no accurate quantitative statement can be made on the subject. The quantity was increased in dogs by poisoning with phosphorus. Perhaps different isomerides of cystin exist, which differ in the readiness with which they give up their sulphur. W. D. H.

Spontaneous Decomposition of Bilirubin. By E. SALKOWSKI (*Zett. physiol. Chem.*, **12**, 227).—In two cases of strongly icteric urine it was noticed that after the occurrence of the ammoniacal fermentation, Gmelin's and Huppert's colour reactions were no longer given. Methods of extraction and precipitation, moreover, yielded no unchanged biliary pigment; dark, amorphous masses only were obtained. This decomposition of bilirubin without the production of any characteristic products, is probably the result of the activity of bacteria, and may probably explain other cases of jaundice in which the urine, though darkly coloured, gave no evidence of bile pigment.

W. D. H.

Poisonous Properties of Dinitroresol. By T. WEYL (*Ber.*, **21**, 512; compare this vol., p. 184).—Doses of 0.054 gram per kilo. body-weight, suspended in a little water or milk, introduced into the stomachs of dogs (of 5 to 7 kilos.), caused in a few minutes great

difficulty in breathing, and convulsions, during which the animals die. Doses of 0.02 gram per kilo. body-weight, dissolved in aqueous alcohol, and applied subcutaneously to moderate-sized dogs, brought on the same symptoms and death in 1 to $1\frac{1}{2}$ hours. Some animals recovered after 3 to 4 hours.

N. H. M.

Chemistry of Vegetable Physiology and Agriculture.

Nitrification of Ammonia and its Salts. By H. PLATH (*Bied. Centr.*, 1888, 6—8).—Frank was led to the conclusion that, although certain species of bacteria may be able to help nitrification in the soil, yet in general the action is produced without the intervention of organisms; he isolated various forms of fungi from the soil, and found that they possessed no power of nitrifying ammonia, also that sterilised soil nitrified ammonium chloride about as quickly as the original soil, and he concluded from some experiments that the calcium carbonate of the soil in presence of water and air produces a slow combination of the nitrogen to nitrous and nitric acids. Dumas (1846) found that by passing moist air and ammonia at about 100°, over chalk for some days, a noticeable quantity of potassium nitrate is formed. Later communications state that this happens also at ordinary temperatures. Millon (1860) asserted that humus had a direct action in nitrifying ammonia.

The author's work aimed at a repetition of that of the above experimenters, and he came to the conclusion that when the action of organisms is eliminated by sterilising soil, neither its individual constituents singly, nor the soil as a whole, can nitrify ammonia, and that, further, the nitrifying power must be due to micro-organisms, and, lastly, that the power of oxidising atmospheric nitrogen cannot be ascribed to calcium carbonate. Frank has since protested against Plath's conclusions, objecting that some important experiments of his were not repeated, and that in order to prove that organisms are the nitrifying agents, Plath has yet to show that the heat employed in sterilising produced no change in the soil other than the death of the organisms.

H. H. R.

Aspidium Felix, Mas. L. By G. DACCOMO (*Chem. Centr.*, 1887, 1357—1358; from *Ann. Chim. Farm.*, **87**, 69—90).—If the ether extract residue of the rootstock of aspidium (male fern) is treated with 2 vols. of 95 per cent. alcohol and 1 vol. of ether, a brown residue is left which is partially soluble in 1 per cent. aqueous potash. The soluble portion is the filicin or filicic acid of Trommsdorff; the insoluble part separates from an alcoholic solution as a white, floccular, waxy substance, $(C_{13}H_{26}O)_n$, melting at 80°, it is insoluble in water, sparingly soluble in ether and cold alcohol, but soluble in hot alcohol; it is not decomposed by boiling alcoholic

potash, and gives no coloration with sulphuric acid and chloroform.

The residue obtained by evaporating the alcohol-ether solution of the original extract, when extracted with water, furnishes glucose and tannin, and with 95 per cent. alcohol a black resin which is almost completely soluble in 2 per cent. aqueous potash. The residue of the extract, insoluble both in water and alcohol, is a green oil difficult to saponify.

The blood-red alkaline solution when agitated with ether parts with some of the red colouring matter (felix red). The residue of this ether extract when distilled with steam furnishes the essential oil of felix; this essential oil appears not to pre-exist in the plant. The residue from this distillation, when extracted with ether, gives, when the ether is evaporated, a red liquid and a precipitate, which, after crystallising from hot alcohol, forms plates melting at 136.5° , having the composition $C_{20}H_{34}O$. This compound has received the name of *aspidol*. It is insoluble in alkalis, easily soluble in ether, benzene, chloroform, light petroleum, and hot alcohol. It is optically active in a 3 per cent. chloroform solution $[\alpha]_D = -24.08$. The filtrate from this precipitate of aspidol was fractionated into three parts. The first fraction, $130-190^{\circ}$, was a yellow oil with a strong odour and acid reaction, which did not reduce silver nitrate. The second fraction, $220-290^{\circ}$, was a beautiful green oil, which gradually became brown; it has the empirical formula $(C_{27}H_{46}O_2)_n$. The third fraction above 300° (at 200 mm. pressure) corresponds with the formula $(C_{34}H_{58}O_2)_n$.

By precipitating the alkaline solution extracted with ether with sulphuric acid, two resins were obtained: 1st, a brick-red solid melting at $85-93^{\circ}$; 2nd, a more abundant and almost black, plastic mass. The filtrate contains butyric acid. J. P. L.

Ensilage Processes. By A. CSERHATI (*Bied. Centr.*, 1888, 39—43). —The value of an ensilage process is determined chiefly by the loss of substance, and by the quantity and nature of the acids produced; the two first items should be as small as possible. The author experimented with various fodders ensiled in glass cylinders or in boxes sunk in the ground. On comparing the merits of fresh fodder with wilted fodder for making silage, he found that the temperature rose slightly higher, and that the loss of substance was greater in the case of the wilted fodder. On comparing the effect of stamping the fodder well down in the silo with only stamping it down round the edges, he found that the temperature rose considerably higher in the latter case. Fry's method of allowing the material to heat and rise to 50° in order to stop the development of micro-organisms, and so to diminish the amount of acid formed is most expensive in loss of material. To see whether such a high temperature was necessary, the author tried stamping the fodders well down, and keeping the temperature under 30° as far as possible. He found that although the amount of acid in the silage was higher than that given by Fry, yet it was in itself very small. He concludes that by proper precautions, namely: having perpendicular walls for the silo; using

fresh fodder; thorough stamping; having a level covering, and heavy weighting, the amount of acid can be kept down without incurring the loss that the employment of Fry's method involves.

H. H. R.

Ensilage in the Open Air. By M. BARTH (*Bied. Centr.*, 1888, 64).—A description of the way a stack of silage was made, and of the composition of the resulting silage.

H. H. R.

Exhaustion of Virgin Soils in Australasia. By R. W. E. MACIVOR (*Chem. News*, 57, 25—26).—The exhaustion of the virgin soils of Australasia is in great part due to the bad system of cultivation giving rise to waste of nitrogen. To grow wheat continuously, the ground is ploughed year after year to a depth of $2\frac{1}{2}$ to 3 inches, thus giving a very shallow surface soil, whilst the continual passage of the shoe of the plough converts the subsoil into a firm compact bed almost impenetrable by the roots of wheat. The surface soil soon becomes dry, and oxidises readily with loss of humus and nitrogen. Another source of loss is the burning the straw. The deficiency of nitrogen is least observed in heavy soils derived from rocks of volcanic origin, then follow those soils traceable to silurian and primitive rocks, whilst light friable soils when in dry and exposed districts are the poorest soils and the greatest sufferers. Soils in New Zealand, Tasmania, and the cooler parts of Australia, contain more nitrogen than soils of the same formation in drier and hotter localities. Dressings of non-nitrogenous manures proved quite useless, and even nitrogenous manures yielded an increased crop without profit. An occasional bare fallow restores matters for a time, but ultimately even that does no good. The introduction of a leguminous crop from time to time has proved beneficial.

D. A. L.

Maintenance and Increase of the Amount of Combined Nitrogen on the Farm. By J. KÖNIG (*Bied. Centr.*, 1888, 16—31).—The first part of this article treats of the natural sources of nitrogen to plants, and discusses the work of previous experimenters bearing on the question; then Hellriegel's investigations are described. He found that the Graminaceæ are dependent for their nitrogen on the combined nitrogen of the soil, and that most probably they only avail themselves of it when it has been transformed into nitrates. In the case of the Papilionaceæ it is quite different. When peas were grown in a soil containing no nitrogen, they first used that which was stored in the seed; when this had all been employed, there was for a time an evident halt in their growth which, however, was only temporary, and they eventually succeeded in supplying themselves with nitrogen from some other source. Their subsequent development varied much in different experiments, although the conditions of growth were the same. To discover whether these variations could be due to the combined nitrogen of the air, one set of plants were grown in ordinary air and another set in air freed from ammonia and nitric acid; the results showed that this was not the cause of the variation, and led to the conclusion that the free nitrogen of the air must somehow become available to the peas. An examination of the roots showed

that at the period when growth was temporarily arrested the so-called leguminous nodules were absent or only in an incipient state, whilst those plants which were growing properly possessed nodules, and that the older and larger the nodules, the better was the development of the plant. These nodules are full of bacteria, and a series of experiments was made, in which to peas growing in soil containing no combined nitrogen there was added, in some cases, an aqueous extract of fertile soil, in others the same extract after sterilisation, and in others again no such addition was made. It was found that the nodules and the thriving of the plant could be produced or prevented at will by the addition or exclusion of micro-organisms.

The growth of lupines on soil containing no combined nitrogen was also investigated, and it was found that they would never attain a satisfactory development when exposed to the same opportunities of receiving germs from the air that enabled some of the peas to thrive; hence it was inferred that the bacteria which occur in the root nodules of lupines are different and less widely diffused than those occurring in peas. This view was supported by the facts that the nodules are different in shape and position on the two plants and contain micro-organisms of obviously different appearance, and also that lupines do not thrive on heavy or rich soil. It was put to the test by growing lupines in sand containing no combined nitrogen, and treating one part of them with an aqueous extract of the soil of a lupine field, a second part with an extract of a clay-marl containing humus and not growing lupines, and leaving a third part without any such addition. All three parts exhibited a period of arrested growth, then the first part started growing and showed nodules like ordinary lupines, the second part showed traces only, and the third part showed no traces of nodules at all.

Of other plants examined, Serradilla (*Ornithopus sativus*) behaved like lupines, whilst vetches and beans (*Vicia faba*) like peas developed best when treated with extract of rich soil; red clover gave no decided result. It thus appears that the Papilionacæ are not dependent on the soil alone for their nitrogen, but that they can make use of the free nitrogen of the air, and that the root nodules and the micro-organisms in them are in close and active relationship to the nourishment and especially to the assimilation of nitrogen by these plants. It must not, however, be inferred that the combined nitrogen of the soil is of no importance to them, for Hellriegel found in some experiments that they could make use of nitrates; although it seems questionable whether nitrates could produce a normal development if micro-organisms were absolutely excluded.

Notwithstanding these researches, it is stated in the article to be still an open question whether the root nodules can change free nitrogen into nitrogenous compounds, although the growth of Papilionacæ is strongly recommended as a means of increasing the combined nitrogen on the farm. To this same end, irrigation by brook and river water is recommended, as a great part of the combined nitrogen dissolved in the water is retained in the form of plant substance.

The second section treats of the ways in which combined nitrogen may be set free and lost, namely: (1) during germination; (2) in

the processes that go on in the animal body (both of which ways have been disputed); (3) during the putrefaction of nitrogenous substances; (4) during the decomposition of organic manures in the soil, especially when it is too strongly aerated by drainage, and nitrification consequently goes on too actively. This section also gives numerous directions for avoiding loss of combined nitrogen in the keeping and employment of manures.

H. H. R.

Manuring Experiments on Oats. By K. MÜLLER (*Bied. Centr.*, 1888, 103—107).—The experiments seem to show that an oat crop following wheat after sugar-beet is grateful for phosphatic and nitrogenous manuring, even when the roots have been excessively manured with phosphates. Chili saltpetre alone produced an increase in grain and straw, the largest increase of grain being caused by the saltpetre in combination with precipitated phosphate, and the lowest by the saltpetre and superphosphate, the greatest increase in straw was produced by an inverted order of phosphates, basic slag holding a middle place in both cases. Placing the expense of manures against the increase in crop, it appeared that saltpetre was the most remunerative, whilst superphosphate and saltpetre together were applied at a loss.

E. W. P.

Increase in Yield of Crops by Nitrogenous Manures. By P. WAGNER (*Bied. Centr.*, 1888, 78—96).—The author draws his conclusions from experiments made by himself, by Märcker, and others; it does not seem that the addition of saltpetre to leguminous crops is of any value, as the increase in yield is so very little, in fact, in some cases there appears to be a decrease in the yield, as the quantity of saltpetre increases. On the other hand, this manure is of value to straws and roots. Employing E. Lierke's tables, Wagner shows how varied is the money value of saltpetre with the different crops in cultivation, and the many circumstances which militate against the complete and successful action of nitrates; to obtain the best result all the necessary plant food must be present in full quantities, to say nothing of want of rain and warmth. The variations in the yield of grain or straw are fully entered on, as well as the causes of such variations. Ammoniacal manures are frequently unsatisfactory, although theoretically the quantity of nitrogen added may exceed that which would be contained in a dressing of nitrate; this probably arises from the fact that the conversion of the ammonia is so slow that the plants do not obtain a sufficiency of nitrate within the requisite time, consequently being "hungered" they are unable to make full use of the other plant foods; it is on this account that ammoniacal manures should be applied to the soil some time before the seed is sown, so that there may be a sufficiency of nitrates present to allow of full, rapid, and unhindered growth.

E. W. P.

Manurial Action of the Free Lime in Basic Slag. By E. JENSCH (*Bied. Centr.*, 1888, 12—16).—The activity of basic slag on soils poor in lime has often led to the free lime in the slag rather than the phosphate being regarded as the active agent. To examine this question six sets of experiments were made with oats grown in pots. A loamy

soil was chosen, and it was used both in its natural state and also after having been treated with dilute hydrochloric acid for some time and then washed. The manures employed were (1) basic slag meal in its original state; (2) basic slag meal which had been treated with sugar solution to remove free lime; (3) lime, and (4) potassium nitrate which was added uniformly to all the pots. The results of the experiments showed that the phosphate in slag from which the free lime had been removed gave nearly as good a yield as in that which still contained free lime, and that although a certain amount of benefit cannot be denied to the free lime, still the increased yield was chiefly due to the phosphate.

H. H. R.

Analytical Chemistry.

Filtration Apparatus. By F. ALLIHN (*Zeit. anal. Chem.*, **26**, 721).—The stem of the funnel has a bulbous expansion, which is ground into the neck of a thick-walled flask. This has a side-tube for connection with the air-pump. M. J. S.

Improved Form of Nitrometer. By G. LUNGE (*Ber.*, **21**, 376—377).—The improvement consists in substituting Friedrich's patent diagonally bored stopcock for the ordinary three-way stopcock of the nitrometer. W. P. W.

Estimation of Iodine. By N. McCULLOCH (*Chem. News*, **57**, 45—48).—Manganic oxide suffers slight reduction in presence of iodine (compare Abstr., 1887, 1141), and therefore titration of iodine by means of alkaline permanganate is inaccurate, and cannot be employed for the determination of iodine in presence of a chloride or bromide, although the latter are not oxidised under the conditions. Hydrogen peroxide is also unsuitable for the purpose. The author therefore proposes to eliminate the chloride and bromide by a process described in the paper in which the mixture containing the chloride, bromide, and iodide is heated with permanganate and strong sulphuric acid, the first two elements are driven off as hydrogen chloride and bromide respectively, whilst the whole of the iodine is oxidised to iodic acid. The solution is diluted, filtered, reduced by means of sulphurous acid, and the iodine determined either by precipitation as silver iodide, or by titration with permanganate in presence of free sulphuric acid and hydrocyanic acid; the latter forms colourless cyanogen iodide with the iodine set free by the sulphuric acid, which would otherwise mask the end reaction. This method of titration is free from the error of reduction of manganic oxide referred to above, and also from the inconvenience of the precipitated manganic oxide accompanying the use of alkaline permanganate. It cannot, however, be used in presence of hydrobromic acid or of the reducing salts of copper, iron, &c.

D. A. L.

Indirect Determination of Fluorine. By S. BEIN (*Zeit. anal. Chem.*, **26**, 733—736; from *Rep. anal. Chem.*, **6**, 169).—The fluorine is expelled as silicon fluoride by heating the substance with powdered quartz and sulphuric acid, and is driven over by a stream of dried air into water. The fluoride and the quartz sand (12 parts) must be very finely ground and intimately mixed. The mixture is placed in a dry flask having a cork through which pass a tube for the admission of dried air, the tube of a separator bulb containing sulphuric acid, and a tube for conveying the gases into water. The last has the outer limb widened. For 1 gram of calcium fluoride, 50 c.c. of sulphuric acid is added and the flask is heated for three hours at 165° with occasional shaking. A further quantity of acid is then added, and the heating and shaking are continued as long as the gas bubbles produce any precipitate. After collecting and washing the silica by suction, it may be at once ignited without previous drying. One part corresponds with 5.494 parts of fluorine. M. J. S.

Estimation of Selenium. By H. N. WARREN (*Chem. News*, **57**, 16).—See p. 435.

Estimation of Nitrites. By A. VIVIER (*Compt. rend.*, **106**, 138—140).—The apparatus is similar to that used in the estimation of nitrites and nitrates by Schloesing's method. The air is first expelled by boiling a small quantity of water in the flask, and the solution of the nitrite is introduced, followed by a solution of carbamide, and finally by dilute sulphuric acid. A current of carbonic anhydride is passed through the apparatus during the whole operation. The mixture is gradually heated and finally is boiled for several minutes, the gas which is evolved being passed through potash solution to absorb carbonic anhydride, whilst the nitrogen is collected and measured. Care must be taken to expel the nitrogen from the flask at the close of the operation by the current of carbonic anhydride. The volume of nitrogen obtained is double that existing as a nitrite.

C. H. B.

Free Acid in Superphosphates. By W. W. MELLON (*J. Soc. Chem. Ind.*, **6**, 803—805).—The average amount of free acid found in 485 samples of manures of various kinds examined was equal to 8.54 per cent. H_3PO_4 ; the highest being 16.36 per cent. and the lowest 2.36 per cent. The results of some experiments are given which show that the amount of free acid and soluble phosphate is affected by the method of extraction adopted, and by the strength of the acid used to decompose the phosphate. The free acid always present in manures seems to consist mainly of phosphoric acid with smaller amounts of hydrofluosilicic acid, hydrofluoric acid and (occasionally) sulphuric acid. The latter was found only in damp samples containing a large amount of free acid. The presence of free hydrofluosilicic and hydrofluoric acids in manures seems to have escaped observation; in the ordinary course of manure analysis, in which the moisture is determined by heating the sample for several hours in the water-bath, they are volatilised and reported as moisture. The average amount of volatile free acids found in 14 samples was

equal to 2.30 per cent., H_3PO_4 , the highest being 3.96 per cent. and the lowest 0.96 per cent. They were estimated by evaporating a solution of the manure to dryness in a platinum dish, the residue was dissolved in water to which a known amount of standard acid had been added, and the solution titrated with standard alkali. The loss of free acid on evaporation equals the total volatile acidity calculated as H_3PO_4 . The amount of free hydrofluosilicic acid found in the 14 samples tested, comprised about two-thirds of the total volatile acidity. The estimation was made by evaporating to dryness a solution of the manure to which some potassium sulphate, neutral to methyl-orange, had been added, the residue being dissolved in standard acid and titrated as before. The increase in the amount of free acid as H_3PO_4 , after evaporation with potassium sulphate, as compared with the amount found on evaporating the solution *per se*, is equivalent to the free hydrofluosilicic acid present. D. B.

Determination of Arsenic as Pentasulphide. By L. W. McCAY (*Amer. Chem. J.*, 9, 174—180).—The tedious precipitation of arsenic pentasulphide according to the directions of Bunsen may be replaced by a very simple, rapid and efficacious method, namely:—the solution containing arsenic acid equivalent to about one to three tenths of a gram of the pentasulphide, is placed in a bottle of 200 c.c. capacity provided with a well-ground stopper; the bottle having been almost filled with freshly boiled water, and the contents saturated with hydrogen sulphide, it is closed, the stopper tied down, and the whole placed in a water-bath for one hour. The precipitate is most easily removed from the bottle, and, the air having been excluded, contains no free sulphur, and does not require to be washed with alcohol and carbon bisulphide. When arsenious acid is treated with hydrogen sulphide in presence of air, but otherwise as above described, it is converted into the trisulphide, no pentasulphide being formed. H. B.

Quantitative Analysis by Electrolysis. By A. CLASSEN (*Ber.*, 21, 359—369).—A simple form of rheostat is described which affords the means of carrying on simultaneously with one battery eight determinations of different metals requiring different strengths of current, and a number of very concordant results obtained by its use are detailed. A new form of voltameter is also described, consisting of a vertical, stoppered, graduated tube expanded at its lower portion into a cylindrical chamber containing the platinum electrodes, which is connected to a second vertical pressure tube by means of india-rubber tubing. This arrangement renders it possible for the gas in the voltameter to be measured at the atmospheric pressure. A description is also given of a stand for the support of the platinum dish forming the cathode and of the anode, whose chief point of novelty consists in the substitution of glass for brass for the material of the rod which supports the arms.

Estimation of Copper in the Presence of Arsenic.—In the presence of more than 0.2 per cent. of arsenic, it has been found impossible in practice to employ the electrolytic method for the deposition of copper

with satisfactory results without previously removing the arsenic by precipitation. This, however, is now unnecessary if the ore has not been roasted, since the whole of the arsenic may be volatilised as arsenic bromide by evaporating it several times on a water-bath with a solution of bromine in hydrochloric acid; the residual bromine compound of copper is then decomposed by ignition with sulphuric acid, dissolved in water, treated with the requisite quantity of nitric acid, and afterwards electrolysed.

Separation of Copper from Lead.—A platinum dish and plate are employed as anode and cathode respectively. To 120 c.c. of the solution containing the two metals, 30 to 40 c.c. of nitric acid (sp. gr. = 1.2) is added, and the resulting solution is electrolysed at first with a current giving in the voltameter 0.1 c.c. of gas per minute, and afterwards, when the lead peroxide has formed a distinct layer on the dish, with a current giving 3 c.c. of gas per minute. At the end of the operation, about 10 c.c. of water is added, the current continued for an hour longer, and then, without interrupting it, the contents of the dish are washed out with water. Treatment with alcohol removes the water adhering to the dish and plate, and these are then dried at 110° until the weight is constant. The lead peroxide adheres firmly to the dish even in quantities of more than 0.2 gram.

W. P. W.

Analysis of Lead Slags. By M. W. ILES (*Chem. News*, **57**, 18—19).—See this vol., p. 418.

Estimation of Thallium. By G. NEUMANN (*Ber.*, **21**, 356—359).—The volume of hydrogen evolved when electrolytically deposited thallium is treated with an acid may be employed as a means of estimating the metal. The thallium salt, together with about 5 grams of ammonium oxalate, is placed in a flask of about 100 c.c. capacity provided with two platinum electrodes 9 sq. cm. in area, and the electrolysis of the slightly warm solution is effected by a current of E.M.F. = 0.1 volt. (?) About 0.6—0.8 gram of the metal, which adheres firmly to the cathode, can be deposited in seven hours, and the end of the reaction is ascertained by testing with ammonium sulphide. Owing to the formation of ammonium carbonate during the electrolysis, it is necessary to remove the liquid in the flask before treating the deposited thallium with an acid; this is effected by drawing a current of water through the apparatus by means of siphons arranged in such a way that contact of the metal with the air is excluded. The electric current is maintained during the washing, and afterwards the contents of the flask are heated to remove occluded gas from the electrodes. The flask is then attached to the author's "hydrometer" (*Abstr.*, 1887, 1140), and the gas evolved on treatment with an acid is measured. The method is applicable to the estimation of the metal in its carbonates, nitrates, chlorides, and sulphates, and the error does not exceed 0.2 per cent.

W. P. W.

Analysis of Iron and Iron Ore. By A. TAMM (*Chem. Centr.*, 1887, 1362; from *Stahl u. Eisen*, **7**, 627—633).—To avoid error in

the determination of phosphorus, the author evaporates the nitric acid solution, which might contain phosphorous acid, to dryness and heats to 200°.

The use of hydrofluoric acid, as recommended by Wood to keep the silica in solution, he regards as superfluous and dangerous, inasmuch as phosphoric acid might be dissolved from the glass. In the case of iron containing manganese, the iron with the phosphoric acid must first be separated with manganese acetate; in the case of iron containing much chromium, complete decomposition only occurs if the quantity of chromium is lessened by fusing together with it iron containing a small but known quantity of phosphorus.

The estimation of sulphur presents difficulties both on account of the possibility of incomplete oxidation of the sulphur and the incomplete precipitation of barium sulphate in presence of ferric chloride. To avoid the latter error, the silica is rendered insoluble by evaporating to dryness, the residue taken up with hydrochloric acid, the solution filtered and again evaporated to dryness, after the addition of barium chloride, and again taken up with hydrochloric acid.

To determine graphite, the iron is dissolved in nitric acid of sp. gr. 1.20, which leaves only graphite undissolved. J. P. L.

Modified Method of Estimating Iron Volumetrically by means of Potassium Dichromate. By H. BYA (*Dingl. polyt. J.*, 266, 606).—In order to reduce the iron to the ferrous state the author, for the sake of rapidity, recommends the use of stannous chloride instead of nascent hydrogen, the excess of reducing agent being removed by the addition of mercuric chloride to the solution previous to the titration with potassium dichromate. D. B.

Determination of Carbon in Steel. By B. BLOUNT (*Chem. News*, 57, 27—28).—The method of determining carbon in steel by dissolving in dilute acid, passing the gases evolved over red-hot copper oxide, and weighing the carbonic anhydride, yields low and irregular results; this the author attributes to the formation of less volatile hydrocarbons, which in the first instance escape being carried over the copper oxide by the gaseous products, and in the second case are filtered off from the solid carbonaceous residue and consequently escape the subsequent chromic acid oxidation; the irregularity being due to slight variations in temperature and in the rate of dissolution. The author suggests as a remedy boiling off most of the water in the flask after solution is complete, and allowing the steam carrying with it the less volatile hydrocarbons to pass over the copper oxide without previous condensation. When methods involving the dissolution of steel in copper sulphate are resorted to, the following plan will expedite the dissolving, and avoid the deposition of copper with the carbon; the steel is placed on a platinum plate forming the positive pole, having a copper negative pole suspended in the liquid, and a current slightly below the strength required for the removal of the copper is passed through; this precaution being taken to prevent oxidation of the carbon. D. A. L.

Analysis of Nickel. By G. LANGBEIN (*Zeit. anal. Chem.*, **26**, 731—732; from *Rep. anal. Chem.*, **6**, 423).—In the electrolytic deposition of nickel from a solution containing manganese, part of the latter may be deposited in the metallic form in company with the nickel. The manganese should therefore be first removed. The nitric acid solution of the alloy (2 grams) is mixed with sulphuric acid and electrolysed for removal of copper. It is then evaporated with more sulphuric acid until fumes of that acid escape. After dilution, excess of ammonia is added and the mixture is kept warm for five or six hours. Since ammonium chloride is absent, the manganese precipitates with the iron, but a little nickel accompanies the precipitate and must be separated by dissolving in warm sulphuric acid and precipitating twice more in the same way. An aliquot part of the solution is then mixed with ammonium chloride and ammonia and electrolysed. Any magnesium present may be determined in the liquid decanted from the nickel.
M. J. S.

Quantitative Separation of Chromium and Uranium. By J. FORMÁNEK (*Chem. Centr.*, 1887, 1407—1408; from *Listy. chem.*, **11**, 217—220).—Separation of chromium and uranium by precipitating the chromium as mercurous chromate in the warm and weighing the chromium as Cr_2O_3 after ignition is not satisfactory, as some uranium is liable to be carried down with the precipitate; on the other hand, some of the mercurous chromate remains in solution if too much acid is present. The mercurous nitrate solution, too, is liable to undergo alteration from oxidation, oxides of nitrogen being formed which reduce the chromate and cause loss. Observing all due precautions, the results are still 1 per cent. too low. If a solution containing uranium and an alkaline chromate is precipitated with soda, the precipitate of uranium should be washed with weak soda, dissolved in hydrochloric acid, and reprecipitated with ammonium sulphide, as recommended by Zimmermann. Ammonia is likely to precipitate some of the alkali as uranate. Ditte's process is not recommended, for not only does uranium remain in solution but the separation of the precipitate of the combined oxides ($\text{Cr}_2\text{O}_3 + \text{UO}_2$), after ignition in hydrogen, cannot be completely effected by means of nitric acid.
J. P. L.

Separation of Tin Oxide from Tungstic Acid. By E. DONATH and F. MÜLLNER (*Monatsh. Chem.*, **8**, 647—649).—The ignited and weighed mixture of tin oxide and tungstic acid is rubbed in an agate mortar with twice its volume of zinc-dust or zinc-filings and turned into a small porcelain crucible. The covered crucible is strongly ignited for 15 minutes, the contents emptied into a beaker, and treated with hydrochloric acid (diluted with two parts of water). It is then boiled until the evolution of hydrogen ceases, and treated with powdered potassium chlorate until the blue tungstic oxide is oxidised to tungstic acid. Water ($1\frac{1}{2}$ vols.) is added to the solution, and it is filtered after 24 hours. The tungstic acid is washed with water containing nitric acid and then with a hot dilute solution of ammonium nitrate; finally it is dried, ignited, and weighed.

The amount of tin oxide can be calculated or may be determined by precipitating the tin as sulphide and weighing as oxide. In this case, zinc-dust must not be used, as it contains cadmium, which would affect the results. N. H. M.

Quantitative Separation of Titanium from Iron. By A. CLASSEN (*Ber.*, 21, 372—375).—The behaviour of titanium trioxide (this vol., p. 424) with alkalis affords a convenient and accurate method of qualitatively and quantitatively determining titanium in the presence of iron, and of all those metals which are precipitated by alkalis; for example, 0.02 per cent. of titanium dioxide in an iron solution can readily be detected by its means. To estimate the quantity of titanium in iron, the usual quantity of material dissolved in hydrochloric acid is freed from excess of acid by evaporation, then treated with 50 c.c. of hydrogen peroxide, and 25 c.c. of aqueous potash, and diluted to a known volume. A wash-water is employed containing 100 c.c. of hydrogen peroxide in the litre and some aqueous potash (sp. gr. = 1.3), and the precipitate is washed by decantation until the washings are no longer coloured yellow on treatment with hydrochloric acid. The precipitated iron is dissolved in the smallest possible quantity of dilute sulphuric acid, converted into the double salt with ammonium oxalate, and estimated by electrolysis; any titanium dioxide or aluminium hydroxide associated with the iron remains in suspension in the liquid. To decompose the hydrogen dioxide, the filtrate from the precipitated iron is heated in a water-bath until the evolution of gas ceases. A portion of the titanium is in this way precipitated as trioxide mixed with some dioxide, and the remainder is precipitated as dioxide by heating the liquid rendered acid with hydrochloric or nitric acid until it is decolorised; ammonia is then added in the smallest possible excess, and the precipitated oxide filtered off, washed, ignited, and weighed. Should the iron or hydrogen peroxide contain silica, it is necessary to moisten the ignited oxide with dilute sulphuric acid, and treat with hydrofluoric acid; the residue is then again ignited. Any alumina can be separated from the precipitate by the ordinary methods (compare Gooch, *Abstr.*, 1885, 1265). W. P. W.

The Air of Sewers. By T. CARNELLEY and J. S. HALDANE (*Proc. Roy. Soc.*, 42, 394—396, and 501—522).—The authors have examined the air of sewers under various conditions. They find that the amount of carbonic anhydride is about twice as great, the amount of organic matter about three times as great as that of the outside air, whilst the number of micro-organisms is considerably less than in ordinary air. These micro-organisms are considered to be derived from the outside, and not from the sewage, (1) from the fact that the ratio between bacteria and moulds is the same as that in the outside air; (2) that the better the ventilation of the sewer, the greater the number of micro-organisms; and (3) because the number of micro-organisms was found to decrease the greater the journey of the air through the sewers, provided always that splashing did not take place. This retention of micro-organisms by the wet sides of the

sewers was proved by means of an experimental sewer. Where splashing occurs, however, a sudden rise in the number of bacteria is found to take place, the bacteria being derived from the sewage itself. The organic matter of the sewer air was almost entirely gaseous, and did not contain anything of the nature of ptomaines.

H. K. T.

Determination of Carbonic Acid in Mineral Waters. By W. BORCHERS (*Zeit. anal. Chem.*, **26**, 720).—In *J. pr. Chem.*, **17**, 353, the author described an apparatus and method for determining successively in one and the same portion of a mineral water the carbonic acid existing in the three forms of metallic carbonate, metallic hydrogen carbonate, and free carbonic acid. The last two are expelled by boiling and the transmission of purified air, the first by adding an acid. It is now recommended to convert the alkaline hydrogen carbonates by the addition of barium chloride into barium hydrogen carbonate, which gives up its second molecule of carbonic acid at a much lower temperature.

M. J. S.

Determination of Phosphoric Acid in Contaminated Waters. By T. L. PHIPSON (*Chem. News*, **56**, 251).—This method can be employed for the detection and determination of very minute quantities of phosphoric acid. About a pint of the water is treated successively with a very small quantity of potash alum in solution, a drop or two of ammonia, and acetic acid until distinctly acid. The precipitate of aluminium phosphate thus formed is dissolved in nitric acid, and the phosphoric acid determined in the usual way.

D. A. L.

Experiments on Heisch's Method for Detecting Sewage Contamination in Water. By F. E. LOTT (*J. Soc. Chem. Ind.*, **6**, 495—499).—The author's experiments completely confirm the observations made by Frankland many years ago, but, being applied to potable waters, they are of some interest as indicating how far Heisch's test may be looked to for information as regards the purity of such waters. On this head, the author's experiments lead him to conclude that—(1.) Any water undergoing butyric fermentation when simply treated with cane-sugar and kept at a temperature of about 26° may at once be condemned as unfit for domestic use. (2.) The single fact of a water not undergoing butyric fermentation is no proof of its purity. (3.) A water which remains clear under this treatment would be less likely to be contaminated by sewage than one which became milky. (4.) The butyric ferment is not perceptibly influenced by the presence of abnormal amounts of chlorine, free ammonia, albuminoid ammonia, sulphates, and nitrates in a water, but is a very accurate indicator of the presence of phosphoric acid.

D. B.

Determination of Ammonia in Arable Soils. By W. KNOP (*Zeit. anal. Chem.*, **26**, 690—699).—A reply to Baumann's criticisms (*Abstr.*, 1887, 82; see also Knop, *ibid.*, 297). The contraction observed when a soil rich in humus is shaken with potash and air is undoubtedly due in part to absorption of oxygen, but not entirely so, since contraction occurs when hydrogen is substituted for air, and

appears to result from the humus occupying less space after than before solution. It may be reduced to an insignificant amount by the use of a large quantity of saturated borax solution. A certain amount of contraction is, however, observed when ferruginous clays free from humus (or freed from organic matter by long boiling with chromic acid) are shaken with strong soda. It is not exhibited by pure kaolin, and possibly may not be by soils containing little iron. In any case, it is complete in five minutes, whereas the contraction due to humus is proportional to the time of shaking. The very large contractions observed by Baumann seem to have resulted from the use of too small a quantity of borax solution, thus both enclosing far too much air in the decomposition flask, and at the same time failing to dilute the hypobromite solution sufficiently. Knop fills the flask to within 40 to 50 c.c., and uses much less hypobromite (10 c.c. to 100 grams) than Baumann seems to have done. To the objection that other nitrogenous substances give up nitrogen when treated with hypobromite, it is replied that from a manurial point of view they may be regarded as equal in value to ammonia, and considering the very small quantity of nitrogenous matter present, the fact that some of these substances do not give up the whole of their nitrogen can only introduce a most insignificant error.

M. J. S.

Estimation of Carbon in Arable Soils. By O. K. STACHOVSKY (*J. Russ. Chem. Soc.*, 1887, 125—132).—In 1882, Dokutschaëff's investigation "On Russian 'Black Earth'" was published, in which this author has shown the distribution and boundaries of arable soil and the "black earth" in Russia. Carbon was determined by Wolff's method, namely, oxidation with chromic acid. In 1883, Loges (*Abstr.*, 1883, 247) investigated Danish soils and found that the results obtained by Wolff's method were too low as compared with those obtained by combustion with copper oxide. The same result had been obtained by Peak and Warrington at an earlier period (*Trans.*, 1880, 617). The author has investigated whether and how far the said difference refers to the case of the "black earth." He uses for oxidation not chromic mixture (the chromic sulphate formed interfering with complete oxidation—the lower numbers found by Loges may perhaps be due to this cause), but an aqueous solution of chromic anhydride. The carbonic anhydride is absorbed in Classen's apparatus (a vertical condenser and two soda-lime tubes). The results obtained by the author with different samples of "black earth" by the chromic acid method agree completely with those obtained by combustion with copper oxide, but of course the first method requires far less time than the second.

When, however, substances containing humous matter, such as peat, were analysed, much lower results were obtained with chromic acid. The author thinks that the good results obtained with Russian "black earth" are probably due to the presence of large quantities of nitrogenous substances in "black earth," which by oxidation are possibly converted into nitric acid and nitrogen oxides; these being good oxygen carriers assist in completing the oxidation of the carbon.

B. B.

Estimation of Grape-sugar in Urine. By H. WILL (*Arch. Pharm.* [3], 25, 812—822).—The urine is mixed with an equal volume of one-fifth normal baryta solution, filtered, and to 5 c.c. of the filtrate another 5 c.c. of baryta solution is added, together with 100 c.c. of 90 per cent. alcohol; after agitation, the solution is set aside for two or three hours. The precipitate is collected, washed with 20 c.c. of 90 per cent. alcohol, and thrown, along with the filter, into the precipitating flask, in which 10 c.c. of decinormal sulphuric acid has previously been placed. After warming and shaking, the excess of sulphuric acid is neutralised with standard baryta solution, using as indicator not more than one drop of phenolphthalein solution (1 : 100). The barium sulphate is now filtered off, and the filtrate is evaporated to dryness and weighed. The grape-sugar remains as a yellowish mass containing a little baryta, which is obtained as carbonate on ignition. This weighing of the sugar serves as a check on the volumetric estimation by means of the baryta precipitate, as described. The author concludes that:—I. Grape-sugar in aqueous solution can be very accurately estimated by the baryta method, either by titrating the baryta or by weighing the separated sugar. II. When baryta in sufficient excess is present, the aqueous solution of the barium sugar compound is precipitated as $\text{BaO}(\text{C}_6\text{H}_{12}\text{O}_6)_2 + \text{BaO}$ on the addition of so much alcohol that the whole mixture contains 81 to 86 per cent. of alcohol by volume. III. In the presence of only 68 to 70 per cent. of alcohol, the precipitate has the composition $\text{BaO}(\text{C}_6\text{H}_{12}\text{O}_6)_2$. IV. In diabetic urine, the results obtained with Fehling-Soxhlet's titration method agree closely with those yielded by the baryta method. J. T.

Formation of Levulinic Acid, a Reaction for the Detection of Carbohydrates. By C. WEHMER and B. TOLLENS (*Annalen*, 243, 314—334).—Most of the contents of this article have already been published (Abstr., 1886, 532). The authors find that levulinic acid is not produced in appreciable quantities when normal urine is heated with mineral acids, showing that normal urine does not contain carbohydrates. W. C. W.

Determination of Tartaric Acid. By F. GANTTER (*Zeit. anal. Chem.*, 26, 714—719).—In carrying out Goldenberg's method (this vol., p. 327), Wiegert (*Zeit. anal. Chem.*, 23, 359) adopts the following precautions. 1. The excess of potassium carbonate should be as small as possible. 2. Acetic acid must be added in corresponding excess. 3. It must be washed out long enough. 4. The acidified mixture must still contain water when the alcohol is added.

To these the author adds that a larger quantity of substance than was originally prescribed must be used. Of argol, lees, or crude calcium tartrate, 10 grams, of residues, 30 grams should be taken, and in both cases one-half of the solution should be used for precipitation. The one or two minutes which is sufficient for the complete decomposition by acetic acid when working with pure substances, is not long enough with crude materials. The evaporation must be stopped at 20 to

30 c.c., the acetic acid added gradually and well stirred in, and the mixture warmed for 15 minutes on the water-bath. M. J. S.

Determination of Tartaric Acid in Wine Lees and Tartar.

II. By A. BORSTRÄGER (*Zeit. anal. Chem.*, **26**, 699—714).—In the experiments in Part I (Abstr., 1886, 1082), the precipitated potassium hydrogen tartrate was always allowed to deposit during the night. A series of comparisons is now made between the results obtained by stirring continuously for 10 minutes and filtering after half an hour, and those yielded by stirring for five minutes and then leaving during the night. The quantity of potassium hydrogen tartrate used was varied from 1.5 to 4 grams, and both 1.5 and 3 grams of oxalate was tried with each quantity of tartrate. Practically identical results (99.51 to 99.72 per cent.) were obtained in all cases.

Grosjean's precaution to prepare the washing liquid exactly at the temperature of the air and to ascertain its actual saturation with potassium hydrogen tartrate by titration, is found to be needless. It suffices to take a hot solution of the tartrate, cool it to about 4° above the temperature of the air, add 10 per cent. of potassium chloride, stir 10 minutes, leave to stand for half an hour, and filter. Even if its temperature differs a few degrees from that of the air it is of no consequence. It should, however, always be freshly prepared.

The following is a more convenient method than Grosjean's for determining the quantity of oxalate required for decomposing the calcium salts. The roughly weighed substance (7.5 grams of lees or calcium tartrate or 3.75 of tartar) is neutralised, and carbonic anhydride is boiled off. Oxalate is then added in quantities of 1.5 grams at a time, heating for 10 minutes after each addition, and testing a filtered sample (acidified with acetic acid) for oxalic acid. Since the amount ascertained in this way can never be more than 1.5 grams in excess, and since any amount between 1.5 and 3 grams is admissible, the amount so employed is increased by 1.5 grams in the actual analysis. In an artificial mixture made to represent lees, and containing calcium sulphate, an hour's heating with the oxalate was found still to leave some of the sulphate undecomposed. A precipitate of calcium oxalate was therefore obtained during the evaporation of the filtrate, and had to be filtered off.

The paper concludes with a minute description of the author's mode of procedure, which, however, only differs from Grosjean's in so far as it embodies the suggestions of this and the previous communications.

M. J. S.

Qualitative and Quantitative Test for Resin Oils in Mineral Lubricating Oil. By L. STORCH (*Chem. Centr.*, 1887, 1419; from *Ber. österi. Ges. chem. Ind.*, **9**, 93—95).—If to one or two drops of resin oil, 1 c.c. of acetic anhydride and a drop of concentrated sulphuric acid are added, a violet colour is immediately produced which soon changes to brown.

The presence of fixed oils or mixtures of fats prevents the reaction. If the presence of resin oil is shown in a lubricant, the quantitative estimation is made as follows:—To a quantity of the oil, five times its volume of 96 per cent. alcohol is added, and the mixture shaken. The

alcoholic solution, which contains the resin oil with a small admixture of the mineral oil, is poured off and evaporated. The residue is weighed and then treated with 10 times its volume of alcohol; any mineral oil undissolved is separated, and the alcohol again evaporated, and the residue weighed a second time. A correction for the amount of mineral oil left in the second residue can be made from the data furnished by the difference in weight of the two residues, and the amount of alcohol used.

J. P. L.

Modified Soxhlet's Apparatus. By J. J. BARLOW (*Chem. News*, 57, 56—57).—In the apparatus described, the substance to be extracted, wrapped in a piece of calico, is suspended from a hook in the flask containing the ether. The flask is fitted with a double-bored cork, carrying two tubes, one short and bent to form a syphon whose longer limb delivers immediately above the substance, the other long and straight; these tubes are enclosed in a wider tube fitting over the cork, and connected with a condenser. The advantages claimed are simplicity, the constant exposure of the substance undergoing extraction to hot ether and hot ether vapour, and the easy recovery of the ether at the close of the extraction.

D. A. L

Determination of Butter in Milk. By H. N. MORSE and W. M. BURTON (*Amer. Chem. J.*, 9, 222—231).—The following improvements are suggested for the process described (Abstr., 1887, 752). The mixture of milk and copper sulphate is ground whilst still somewhat moist, and in filling the extraction tube, the mixture is packed somewhat tightly by use of a glass rod. Treatment two or three times with light petroleum (15 c.c. each time) is ample for the extraction of the fat. The light petroleum solutions are heated on the water-bath for 20 minutes with so much potash dissolved in alcohol as will saponify 0.1 gram of butter, and finally the excess of alkali is estimated with hydrochloric acid, using phenolphthaleïn as indicator.

Light petroleum, boiling at 45—60°, is as efficacious as that boiling at 30—45°; it is not necessary to remove the petroleum before saponifying; from the examination of a number of samples, it is shown that practically identical results are obtained by weighing the fat extracted, or by saponifying, or by conducting the whole operation as above, and that the amount of alkali required to saponify a given weight of butter is very constant; the variations noticed by Koettstorfer (0.2215 to 0.2324 gram potassium hydroxide per gram of butter) are due to the fact that when butter is fused and allowed to cool without agitation, a partial separation of the constituents takes place, and the mass is not homogeneous. The authors find that 0.02295 gram of potash is required for 0.1 gram of butter.

H. B.

Determination of the Dry Residue and Fat in Milk and Butter. By F. GANTTER (*Zeit. anal. Chem.*, 26, 677—680).—As a porous material for absorbing the milk to be dried, the author prefers wood-fibre, such as is prepared for the manufacture of paper. It requires to be washed with light petroleum. About 2 grams are placed in a capsule, dried at 105°, and weighed together with a small

glass rod. Being very hygroscopic, a cover is necessary. The milk (5 or 6 grams) is poured on the fibre, avoiding as far as possible any wetting of the capsule, and during the evaporation the fibre is stirred occasionally in such a way as to wipe the capsule clean. After one hour, it can be transferred to the drying oven, where $1\frac{1}{2}$ hour is long enough for drying the residue from 6 grams of even a very rich milk. The fibre is then removed from the capsule, wrapped in paper, and extracted in Soxhlet's apparatus with light petroleum. Here two hours' extraction is found to be sufficient. In determining the water in butter, 3 grams of fibre should be used for 5 grams of butter. Owing to the large surface exposed, a constant weight is obtained after $1\frac{1}{2}$ hours' drying. M. J. S.

New Method of Examining Butter. By T. T. P. B. WARREN (*Chem. News*, 56, 262; compare this vol., p. 199).—Both cotton-seed oil and cocoa-nut oil were found in a sample of oleomargarine, although the latter was free from taste and smell; subsequent experiment showed that by mixing cocoa-nut oil with a certain quantity of cotton-seed oil, its odour and taste are concealed; when, however, these two oils are present in oleomargarine, the animal fats separated from them have a strong, rancid odour. It is noteworthy that when cocoa-nut oil alone is treated with carbon bisulphide and sulphur chloride, it behaves like butter; but when mixed with most fats or oils it is not so easily acted on by sulphur chloride, unless in large excess; by applying the author's method (*loc. cit.*) to an experimental mixture, containing 1 part of cocoa-nut oil to 3 parts of cotton-seed oil, the former oil was recovered perfectly white and solid. An example is given of the working of the method, applied to the analysis of an oleomargarine containing cotton-seed oil; and in two test experiments with the cotton-seed oil (as used in the analysis) alone, solid residues were obtained differing from one another by 5 per cent.; in the author's opinion, however, the difference need not be so great after a little practice. D. A. L.

Action of Sulphur Chloride on Oils. By T. T. P. B. WARREN (*Chem. News*, 57, 26—27, 43).—The result produced by this reagent with linseed oil depends on the quality and quantity of the chloride, on the temperature at which the mixing is made, and on the quality and quantity of the solvent. If the solvent is volatile, inactive, and in excess, the reaction only starts when the sulphur chloride solution becomes sufficiently concentrated by the evaporation of the solvent. If the solvent is not volatile, the sulphur chloride reaction seems to be arrested or modified. Small quantities of sulphur chloride will merely thicken linseed oil owing to the altered oil dissolving in the un-attacked oil, although oil once perfectly acted on will not dissolve in fresh oil. When analysing a mixture of drying with non-drying oils by means of sulphur chloride, it is well to add enough of a known oil to make the combined quantity of known and drying oil relatively large as compared with the non-drying oil. Under exactly similar conditions of experiment, a drying oil will yield constant quantities of a solid product insoluble in carbon disulphide; in the same way

turpentine, resin oils, and mixtures of these yield products soluble in carbon bisulphide or heavy petroleum, therefore these latter oils can be readily separated from drying oils by sulphur chloride. As excess of sulphur chloride produces a less solid product than when such excess is avoided, this must be taken into consideration when treating unknown oils. In dealing with mixtures of oils in which each individual oil gives a solid product, the results obtained are only approximate, and must be verified by treatment of a known mixture of the oils. The author then indicates the very extensive amount of adulteration and substitution of inferior for superior oils in commerce, which can be detected by means of sulphur chloride. D. A. L.

Estimation of Urea by Titration. By T. PFEIFFER (*Zeit. Biol.*, **24**, 336—350).—This paper is a lengthy reply to the criticisms recently passed by Pflüger (this vol., p. 201) on Pfeiffer's modification of Liebig's method of estimating urea. W. D. H.

Titration of Pyridine Bases. By K. E. SCHULZE (*Ber.*, **20**, 3391).—5 c.c. of pure pyridine (sp. gr. 0.98) was dissolved in 100 c.c. of water; 25 c.c. of the solution was treated with 1 c.c. of 5 per cent. aqueous ferric chloride solution; normal sulphuric acid solution was then carefully added until the precipitated ferric hydroxide redissolved. The amounts actually used were 15.5, 15.4, and 15.5 c.c.; 15.5 c.c. being the amount required by theory. γ -Picoline was titrated in a similar manner. N. H. M.

Volatile Alkaloids. By O. DE CONINCK (*Compt. rend.*, **105**, 1258—1260).—A description of colour and other reactions of the pyridic alkaloids.

Improved Method of Estimating Caffeine in Coffee. By E. D. SMITH (*Chem. Centr.*, 1887, 1270—1271; from *Zeit. öster. Apoth. Ver.*, **41**, 359).—To determine caffeine, 0.65 gram of coarsely powdered coffee is mixed with 0.13 gram of magnesia, boiled with 150 c.c. of water for five minutes, filtered, and the filtrate made up to 200 c.c. by percolation; the residue is again boiled for five minutes with 100 c.c. water, filtered, and this filtrate made up to 300 c.c. by percolation. The combined filtrates are evaporated to 20 c.c., the residue treated with 120 c.c. of strong alcohol, the precipitate filtered and washed with alcohol, the alcohol driven off, and the residue dissolved by the gradual addition of small quantities of water. This solution is extracted three times with 25 c.c. of chloroform. On evaporating the chloroform, crystalline caffeine is obtained. J. P. L.

Estimation of Theine in Tea. By B. H. PAUL and A. J. COWNLEY (*Pharm. J. Trans.* [3], **18**, 417—419).—The authors recommended the following method of estimating theine (caffeine) in tea:—5 grams of the powdered tea is moistened with hot water, mixed with 1 gram of calcium hydroxide, and dried on the water-bath. The residue is then extracted with strong alcohol in a small percolator. The alcohol is removed from the filtrate by evaporation, and the residual aqueous

solution mixed with a few drops of sulphuric acid, filtered, and the filtrate shaken in a separator with about 200 c.c. of chloroform, which is used in six successive portions, the last being tested to ascertain that all the theïne has been taken up. The whole of the chloroform solution is then shaken in a separator with a very dilute solution of aqueous soda, by which it is completely decolorised; the chloroform extract is evaporated in a tared flask, and the residue weighed.

The authors have found in Indian and Ceylon teas a higher percentage of theïne than has usually been supposed to exist, varying from 3.22 to 4.66 per cent. on the air-dried substance. The amount of theïne had no relation to the commercial value of the 28 samples examined, the prices of which ranged from 7*d.* to 7*s.* per lb. The numerical results are given in a table. The method used by dealers in testing tea (tasting) is described. The value is not indicated by the amount of extract obtained by boiling water.

R. R.

Estimation of the Alkaloids of Conium. By R. A. CRIPPS (*Pharm. J. Trans.* [3], **186**, 511—512).—In place of the troublesome and inaccurate distillation methods, a process is described based on the extraction of the finely powdered fruits with a mixture of alcohol, chloroform, and a chloroform solution of hydrogen chloride, and the conversion of the bases in the extract into the hydrochlorides, in which form they are weighed.

A. J. G.

Determination of Tannin. By F. GANTTER (*Zeit. anal. Chem.*, **26**, 680—682).—The author has made comparative determinations of tannin in a variety of tanning materials by the method of the German Tanners' Association (known as the 1 c.c. method), using on the one hand hide powder, and on the other the N/10 solution of ferric acetate recommended by E. B. (Abstr., 1887, 311). In almost every case, the latter gave the lower result, and from the fact of the quantity of substance taken being varied according to its richness, the differences are inversely proportional to the weights employed. In a nearly pure tannin, the difference amounted to 10 per cent. Unless, therefore, it can be shown that the precipitation by hide powder gives incorrect results, that by ferric acetate cannot be substituted for it.

M. J. S.

Hoppe-Seyler's Soda-test for Carbonic-Oxide-Hæmoglobin. By E. SALKOWSKI (*Zeit. physiol. Chem.*, **12**, 227—228).—The following method of performing the test is suggested:—The blood in question is diluted 20 times, and to some of this in a test-tube an equal volume of aqueous soda of sp. gr. 1.34 is added. In a few seconds, carbonic oxide blood becomes whitish, then red; on standing, red flocculi separate, and finally rise to the surface of a faintly rose-coloured liquid. In normal blood, all that is produced by the addition of the alkali, is a dirty-brown coloration. After standing 20 hours, the precipitate in both cases is redissolved, and the clear red liquid shows almost the same absorption-bands as those of oxy-hæmoglobin.

W. D. H.

General and Physical Chemistry.

Refraction of Liquids between wide Limits of Temperature.
By E. KETTELER (*Ann. Phys. Chem.* [2], **33**, 353—381 and 506—534).—As none of the expressions hitherto proposed for the refraction of liquids at different temperatures are found satisfactory, the author has from theoretical considerations deduced a relation between refraction and temperature, and tested the same experimentally. The first part of the paper is devoted to a description of the apparatus used and the method of working, in the second are the results of the experiments and a discussion of the same. The liquids examined were water and alcohol. The refraction in every case was measured for the sodium, lithium, and thallium lines.

The refraction of water between 0° and 20° having already been measured by Rühlmann, the present experiments were conducted for the interval 20° to 95° , a large number of observations at intermediate temperatures being made. The formula proposed by Rühlmann for the refractive index, $v = v_0 - at^2 + bt^4$, is found to be in fair agreement with the observed values up to 85° . A much better agreement is, however, obtained by the use of the author's proposed formula

$$(n^2 - 1)(v - \beta) = C(1 + \alpha e^{-kt}) = M,$$

where $C = (n^2 - 1)v = 0.62035$, is taken from Lorenz's measurements for water-vapour and the sodium line. Also, since it is now proved that the dispersion for liquids follows the same law as that for gases, $\frac{n_a^2 - 1}{n_\beta^2 - 1} = \text{const.}$, where for the same density α and β represent two different coloured rays; the constant C will alone alter with the nature of the light of which the other constants will be independent. For the lithium and thallium lines, C has the values 0.61574 and 0.62428. The equation is also satisfied by two series of values for the other constants, β , α , and k .

$$\begin{array}{lll} (1) \quad \beta = 0.20271 & \alpha = 0.00246 & k = 0.02290 \\ \text{or } (2) \quad \beta = 0.15999 & \alpha = 0.05617 & k = 0.000937 \end{array}$$

Both these series give values agreeing very well with the experiments, and the two agree well together up to 100° . For the latter series, k is so small that its higher powers may be neglected, and we get $M = C \{1 + \alpha(1 - kt)\}$, or the law of refraction takes a linear form with regard to t : $(n^2 - 1)(v - \beta) = c - \gamma t$.

For alcohol, the experiments extend from -7.85° to $+76.34^\circ$. A law similar to that in the case of water holds good. It is, however, not continuous, and two portions of the series have to be distinguished. Between $t = 33.69^\circ$ and $t = \infty$ we get $M = C(1 + \alpha e^{-k(t - t_0)})$, where the value of C for the lithium, sodium, and thallium lines is 0.84198, 0.84750, 0.85249; $t_0 = 33.69^\circ$, $\beta = 0.200$, $\alpha = 0.07748$, and

$k = 0.002215$. From $t = -10^\circ$ to $t = 33.69^\circ$, we get the simpler law $M = C(1 + \alpha)$, the value of which is 0.91317 for the sodium line.

In each case, the experiments prove that the dispersive power for the liquid and gaseous states is the same. H. C.

A New Method for Determining the Rotatory Dispersion of an Active Substance and a Case of Anomalous Dispersion. By G. H. v. WYSS (*Ann. Phys. Chem.* [2], **33**, 554—569).—The spectrum from ordinary white light is directed into a polarising apparatus by means of a collimator, the slit of which is adjusted to allow successively the passage of rays from each portion of the spectrum. The wave-lengths of the rays are calculated by means of Cauchy's formula. In this way, the rotation for different portions of the spectrum and for known wave-lengths is obtained.

A sample of turpentine thus examined was found to be feebly lævorotatory. It gave for $\lambda = 661$ a rotation of 3.0815° . As the wave-lengths decreased, the rotation increased and reached a maximum of 3.3688° for $\lambda = 565$. The rotation now, however, began to decrease on approaching the blue end of the spectrum, and for $\lambda = 494$ was only 2.9976° .

This behaviour is contrary to Biot's law that the rotation of a ray is inversely proportional to the square of the wave-length, an exception to which, however, had already been observed by Biot and Arndtsen in the case of tartaric acid, the latter concluding that the sample examined was probably a mixture of lævo- and dextro-rotatory acid. As it was quite possible that the present anomaly might arise from a similar cause, mixtures of dextro- and lævo-turpentines in different proportions were examined, and it was indeed found that a mixture containing about 68 per cent. of dextro-turpentine behaved in a manner exactly similar to the above. H. C.

Comparing Spectra. By E. F. J. LOVE (*Phil. Mag.* [5], **25**, 1—6).—In order to discriminate coincidences between lines of different spectra, a method based on the law of error is made use of, in which the differences between the wave-lengths of the compared lines are divided into groups according to the magnitude of the difference. A curve is then plotted having the number of observations in a group for an ordinate, and the average error of the group for an abscissa. The curve is compared with that given by the equation $y = ae^{-c^2x^2}$, and any large discrepancies noted. The above law supposes the errors to be of every magnitude and infinite number, hence the observed curve will be steeper than the theoretical one. Comparisons by this method of spectra of the same element obtained by different observers give curves which agree closely with the curve of error, whilst that obtained by a comparison of iron with nickel and titanium is widely divergent. A comparison between the arc-spectrum of cerium and the widened lines of a sun-spot spectrum gave a curve closely resembling the above test curves. Grünwald's comparison (Abstr., 1887, 1070) between the wave-lengths of the water-spectrum as deduced

by him from those of hydrogen and their values as obtained by observation, is examined. The curve obtained agrees almost exactly with the theoretical curve except at four points. Finally, a comparison between the spectrum of Grünwald's constituent "b" of hydrogen and the nearest solar lines gives a curve which agrees with theory except at two points. The discrepancies in the two last comparisons seem to point to a small systematic difference, probably between the scale of measurement of the hydrogen spectrum and Ångström's scale.

H. K. T.

Modifications in the Absorption-spectrum of a Substance.

By F. STENGER (*Ann. Phys. Chem.* [2], **33**, 577—586).—The absorption of light by any substance of definite chemical composition is assumed to depend on the size of the physical molecules of that substance in the condition in which it is examined. Hence as long as the molecular aggregation remains the same, whatever condition the substance be in, the absorption-spectrum will be the same, but an alteration in the molecular aggregation will bring about an alteration in the absorption-spectrum.

Iodine dissolves in carbon bisulphide to a violet, in alcohol to a brown solution. As the colour of the carbon bisulphide solution approaches more nearly to that of iodine vapour than that of the alcoholic, it may be assumed that in the first the molecules are in a simpler state of aggregation, and this view is supported by Wiedemann's observation that when the carbon bisulphide solution is cooled by means of ether and solid carbon dioxide, the colour changes to brown.

Magdala-red has a very different absorption-spectrum in alcohol, in which it is very soluble, to that which it shows in water, benzene, toluene, xylene, turpentine, or carbon bisulphide, in which it is only sparingly soluble. By mixing any of the latter solvents, however, with alcohol in different proportions, the absorption-spectrum of the one may gradually be converted into that of the other. The molecular aggregation in the first case where the substance is readily soluble is probably simpler than in those in which it is sparingly soluble.

Vogel (*Berl. Monatsber.*, 1878, 409) has shown that when a solution of a coloured substance or salt is evaporated on a glass plate, the absorption-spectrum of the solid obtained is very different from that of the solution. This alone greatly supports the view as to the influence of molecular aggregation. The author shows that if the solution be mixed with collodion, gelatin, or starch-paste and then evaporated, the character of the absorption-spectrum does not alter with the change from the liquid to the solid state. The above substances would appear to keep the molecules apart when drying, and prevent further aggregation taking place.

The above also holds good of those substances which show fluorescence in the liquid but not in the solid state. If solutions of such substances in gelatin be evaporated, the film fluoresces strongly even after it has been kept for some time. As fluorescence probably depends on the smallness of the physical molecules of the fluorescent substance, this further supports the author's views.

H. C.

Fluorescent Mixtures. By L. DE BOISBAUDRAN (*Compt. rend.*, 452—455).—The author withdraws the statements made in *Compt. rend.*, 105, p. 1231, lines 19—33, and p. 1232, lines 1—4. The quantities of chromium oxide given on p. 1229 are four times as great as they should be.

Purified calcium oxide shows distinct although not very strong greenish or bluish-white fluorescences, which are usually of short duration, and show no spectral bands. These fluorescences are much feebler after the calcium oxide has been strongly heated in hydrogen. Some specimens show a rose fluorescence which is not affected by heating in hydrogen.

Comparatively pure calcium carbonate was dissolved in hydrochloric acid, and fractionally reprecipitated. The first fraction showed a rose fluorescence, becoming blue-violet when heated, the manganese band being readily recognisable; the second fraction gave a blue-violet fluorescence, whilst in succeeding fractions the fluorescence became weaker and weaker. It would seem from these results that the fluorescence of calcium oxide is due to the presence of minute quantities of impurities. C. H. B.

Galvanic Polarisation. By F. STREINTZ (*Ann. Phys. Chem.* [2], 33, 465—474).—In continuation of his experiments on the above (this vol., p. 99), the author has examined the polarisation of mercury, gold, palladium, and platinum electrodes. With mercury, the polarisation of the hydrogen plate is at a maximum when the E.M.F. of the cell used is that of two Daniells, and for further increase remains constant. This maximum is higher than that observed for any other metal. The polarisation of the oxygen plate varies with the time of immersion, and continually increases with the E.M.F. of the cell used. With the three other metals, the results agree generally with those of Fromme (*Abstr.*, 1887, 541). When the intensity of the current used is greater than that required to produce maximum polarisation, in each case a decrease in that of the oxygen plate sets in, that of the hydrogen plate remains constant in the case of platinum, but shows a variation with the time of immersion for gold and palladium. H. C.

Conductivity of Illumined Air. By S. ARRHENIUS (*Ann. Phys. Chem.* [2], 33, 638—644).—It is shown that air under a pressure of 1 to 20 mm., when illumined by the sparks of an electrical machine, acts as a conductor, the maximum conductivity being for a pressure of 4 to 5 mm. This conductivity is shown to be electrolytic, as a current may be obtained flowing from a zinc to a platinum plate in illumined air, just as it would were these plates immersed in water. No manifestation of the above could be obtained for pressures other than those stated, although the author considers that it is not confined within those limits. In support of this he quotes the experiments of Hertz (*Ann. Phys. Chem.* [2], 31, 983), in which it was shown that sparks are more easily formed in air at the ordinary pressure when the path is illumined than when it is kept in the dark. H. C.

Molecular Conductivity of Fuming Nitric Acid. By E. BOUTY (*Compt. rend.*, **106**, 595—597).—Fuming nitric acid, which always contains a slight excess of water, dissolves large quantities of potassium nitrate, forming compounds which can be crystallised, and the solutions behave with respect to conductivity like aqueous solutions of very soluble salts. The conductivity of the acid at first increases more rapidly than the proportion of dissolved salt, attains a maximum, and then decreases as the solution becomes more viscous. With small quantities of salt, the increase in conductivity is proportional to the weight of salt dissolved.

Sodium nitrate is only slightly soluble in nitric acid, and does not form crystallisable compounds. The nitric acid solution, like the aqueous solution, behaves abnormally, and has a higher resistance than similar solutions of other nitrates.

The unit of conductivity in these experiments was the resistance of normal nitric acid. The nitric acid used was of sp. gr. 1.552. A molecular resistance of 15.72 ohms is the limit of conductivity of the solutions of potassium and ammonium nitrates in nitric acid. This value approximates very closely to the molecular resistance of potassium chloride in aqueous solution. The resistance of solutions of nitrates in nitric acid increases rapidly on addition of water.

C. H. B.

Electrical Resistance of Bismuth and its Alloys. By E. v. AUBEL (*Phil. Mag.* [5], **25**, 191—201).—The electrical resistance of bismuth and its alloys in a powerful magnetic field is determined. The bismuth was prepared in three forms—(1) melted and cooled slowly; (2) melted and cooled quickly; (3) compressed. The first was obtained by melting the metal in capillary tubes immersed in sand; for the second the metal was melted and poured into a V-shaped iron mould; the third was prepared by Spring's method. The alloys were prepared by mixing weighed quantities of the metals. The resistances were measured by Thomson's method, and the results show that in some samples of bismuth the resistance rises, in others falls, with rise of temperature. The experiments with alloys show that this is not due to the presence of tin or arsenic as an impurity, nor was there any relation shown with their fusing points or specific gravities. Magnetism produces an increase in resistance, but the effect is feeble. Compressed bismuth shows hardly any alteration in resistance with change of temperature, but if it is fused and cooled slowly the usual effect is observed. In the compressed bismuth which had been drawn through a draw-plate, the particles form parallel fibres.

H. K. T.

Electrolysis of Copper. By T. GRAY (*Phil. Mag.* [5], **25**, 179—184; compare *Abstr.*, 1887, 315).—The electrochemical equivalent of copper is determined for varying current-densities. The copper sulphate solutions had a density of 1.15 to 1.18, and were always acid. The plates were cleaned with glass-paper, and after deposition were washed with acidified water and dried before a fire. At temperatures of 10—15°, the results are constant, but the loss in weight of the plate increases rapidly as the temperature rises to 35°. The

error can be ascertained within 0.1 per cent. by keeping a similar plate in a cell with no current passing through it. At 2°, there is no change in the amount of metal deposited until the area of the plate exceeds 200 sq. cm. per ampère. A table of apparent electrochemical equivalents of copper for different current-densities and temperatures is given.

H. K. T.

Thermal and Electrical Behaviour of some Bismuth-tin Alloys in the Magnetic Field. By A. v. ETTINGSHAUSEN and W. NERNST (*Ann. Phys. Chem.* [2], **33**, 474—492).—The authors were led by former experiments to suspect some connection between the thermoelectrical properties of metals, and the “rotatory power” in a magnetic field observed by Hall (*Phil. Mag.*, 1885, **19**, 419). Since the thermoelectrical properties of bismuth are greatly modified by alloying with tin, the present investigations were undertaken with the object of ascertaining whether this modification would be attended with similar change in the rotatory power. A series of four alloys containing varying amounts of tin were examined, but although the rotatory power was very largely influenced by the presence of the tin no definite connection with the thermoelectrical properties could be traced.

H. C.

The Recalescence of Iron. By H. TOMLINSON (*Phil. Mag.* [5], **25**, 103—116).—The internal friction of iron at different temperatures is determined by suspending a wire vertically and noting its period of horizontal vibration, the wire being heated by an electric current. A table of results is given. At 550° the internal friction rises rapidly, and still more rapidly at 1000°, so that at this temperature the wire comes to rest after two or three vibrations. From 1100° to 1200° it seems to decrease. At 550° the magnetic and thermoelectric properties also change. At 1000° heat also becomes latent, as shown by alterations at this temperature due to stress and strain. The author considers that recalescence is similar to regelation, being a sudden evolution of heat at temperatures somewhat below these points. When iron has been strained either by bending or hammering, the strained portion as the iron cools appears clouded, owing to the more rapid cooling of the strained portion, its specific heat being less than that of the unstrained parts, probably because the consumption of heat in separating the particles is prevented by the strain. Shortly before recalescence, the cloud disappears. Recalescence does not seem to be prevented by shaking or hammering. With well annealed iron, recalescence cannot be detected. The author considers that it does take place, but at a point near the critical temperature (1000°), and hence is not visible.

H. K. T.

Evaporation of Liquids. By W. HEMPEL (*Ber.*, **21**, 900—902).—Liquids can be evaporated about six times more rapidly (with, however, the combustion of about three times the amount of gas per hour) than on a steam-bath by employing a Siemens' inverted regenerative burner placed just above the surface. The liquids do not enter into ebullition, so all spirting is avoided. Experiments show

that no appreciable amount of sulphuric acid is absorbed by the liquids during evaporation, and that whilst hot the iron parts of the burner are not attacked by acid vapours.

W. P. W.

Bumping during Distillation. By A. REISSMANN (*Arch. Pharm.* [3], 25, 970; from *Pharm. Centralb.*, 28, 501).—A closely wound platinum spiral is charged with several longish bits of pumice, and its ends are then closed. One or more of these spirals placed in a liquid undergoing distillation effectually prevents bumping, and the operation goes on with perfect regularity. The platinum must be heavy enough to sink the pumice.

J. T.

Relation of Gases to Mariotte's Law at High Temperatures.

By C. PUSCHL (*Monatsh.*, 9, 93—98).—If at ordinary temperatures the volume of a liquid be v and the pressure p , pv increases with the pressure, so that $d(pv)/dp = h$ is positive. If t be the temperature, and α the coefficient of expansion of the liquid, then $dh/dt = d(\alpha pv)/dp$, so that by following the change in h with temperature, the change in pv or in Mariotte's law may be ascertained.

At pressures above the critical, heating the liquid gradually to above the critical temperature, the quantity h will be found to pass through two maxima with one minimum in between, and the latter if the pressure be continually increased at high temperatures will change from negative to positive values, and may in the end be brought into coincidence with the higher maximum, which at the same time falls to lower temperatures. If the pressure then were high enough, h would, from the lower maximum, continually decrease with rise of temperature.

For pressures below the critical, h is negative and increases with the temperature. This is the case with all gases and vapours, with the exception of hydrogen. If heated, then, a point $h = 0$ will be reached at which the gas will obey Mariotte's law. Above this point, h takes a positive value, reaches a maximum, and then falls again, it crosses the zero-line a second time, and becomes permanently negative.

There is also for every gas an interval of temperature for which h is positive at every pressure, and pv has neither maximum nor minimum. On each side of this interval, there are two pressures for every temperature at which $h = 0$, for the smaller of which pv is a maximum and for the greater a minimum. At the higher and lower limiting values for these temperatures the two pressures will coincide.

H. C.

Easy Method of Finding the Specific Gravity of Liquids.

By A. B. TAYLOR (*Chem. News*, 51, 138—139).—For the sake of simplicity, the author suggests that the weight of a convenient solid should be so adjusted that, expressed in grains, it corresponds with its sp. gr., then, on weighing it in the liquid to be tested, the loss of weight in grains will give the sp. gr. of that liquid without calculation.

D. A. L.

Compressibility of Water. By W. C. RÖNTGEN and J. SCHNEIDER (*Ann. Phys. Chem.* [2], **33**, 644—660).—The authors repeat their experiments on the above (*Ann. Phys. Chem.* [2], **29**, 197), using greater pressures, and thus obtaining a greater contraction. The apparatus, with the exception of a new manometer, is that previously used. Experiments were conducted at the temperatures 0° , 9° , and 17.95° , and gave as the apparent compressibility per atmosphere at these temperatures 0.00004910, 0.00004602, and 0.00004413. The experiments being made with great care, and account taken of all known sources of error, the last figure only in the above is looked on as doubtful. The constant of deformation of the piezometer was determined by comparing the observed apparent compressibility of rock salt with the true compressibility obtained by Voigt (*Ber.*, 1884, 990); by introducing this correction, the true compressibility of water at the above temperature is obtained. This is 0.0000462 at 17.95° , a value which exactly agrees with that obtained by Grassi, 0.0000481 at 9° , and 0.0000512 at 0° .
H. C.

Decrease in the Solubility of Sulphates. By A. ETARD (*Compt. rend.*, **106**, 206—208).—At temperatures below 100° , the solubility of cupric sulphate increases with the temperature, but between 103° and 190° the solubility diminishes as the temperature rises. This deflection in the curve of solubility is observed with almost all sulphates. With cadmium, zinc, manganese, and iron sulphates, the point of deflection is below 100° . A similar decrease in solubility is observed in the case of salts of carbonic, sulphurous, and succinic acids, but not with salts of monobasic acids, except those of feeble organic acids.

In the case of zinc sulphate, $y = 27.6 + 0.2604t$ between -5° and 81° , and $y = 50.0 - 0.2244t$ between 81° and 175° . At 180° , the solubility is the same as at -5° . As the temperature of a saturated solution rises, the hydrate $\text{ZnSO}_4 + 2\text{H}_2\text{O}$ is deposited on the sides of the vessel in hard, insoluble, porcelain-like concretionary masses. At all temperatures there is, in all probability, a condition of equilibrium between this and the other hydrates existing in the solution.

In the case of manganese sulphate, $y = 30.0 + 0.2828t$ between -8° and 57° , and $y = 48.0 - 0.4585t$ between 57° and 150° . The solution deposits anhydrous manganese sulphate as a hard, rose-coloured, porcelain-like mass, almost insoluble in water. The equation indicates that the solubility vanishes at 161° , and experiment shows that at 180° the liquid retains mere traces of the salt.

For potassium sulphate, $y = 7.5 + 0.1070t$ between 0° and 163° , and between 163° and 220° the solubility remains constant.

C. H. B.

Laws of Chemical Equilibrium. By H. LE CHATELIER (*Compt. rend.*, **106**, 355—357).—A mathematical paper, not admitting of useful abstraction.

Chemical Equilibrium. By P. DUHEM (*Compt. rend.*, **106**, 485—487).—The results obtained by Le Chatelier are identical with those obtained by the author (*Compt. rend.*, **99**, 1113).

Laws of Chemical Equilibrium. By H. LE CHATELIER (*Compt. rend.*, 106, 598—601).—The author points out that there is an essential difference between his views and those of Duhem.

C. H. B.

Explosion of Water Gas. By A. v. OETTINGEN and A. v. GERNET (*Ann. Phys. Chem.* [2], 33, 586—609).—The gas generated electrolytically was passed without previous drying into the eudiometer, and by means of a rotating mirror photographs of the course of the explosion were taken, small quantities of metallic salts being used to colour the flame. The results show that in accordance with Bunsen's view, the total combustion takes place in successive partial explosions. Each explosion causes a wave which travels along the tube, and the meeting of two such waves gives rise to secondary waves, as appears from the photographs. The rate of explosion measured was 2800 metres per second, which agrees approximately with the value obtained by Berthelot.

H. C.

The Carbon-atom and Valency. By V. MEYER and E. RIECKE (*Ber.*, 21, 946—956).—The theoretical conclusions of van't Hoff and Wislicenus have not only been supported but also extended by the experiments of Meyer and others on the isomeric benzildioximes; the result of which is, that to the hitherto generally accepted properties of the carbon-atom, the following two must be added:—(1) The four valencies of the carbon-atom can be diverted from the regular tetrahedric direction in which they are supposed to exist in marsh-gas, and compounds of the constitution Ca_4 ; (2) There are two ways in which two singly-bound carbon-atoms can be united, one which allows free rotation in various directions, one which does not.

On various chemical and physical grounds, the authors put forth the following hypothesis on the constitution of the carbon-atom:—The carbon-atom is surrounded by an ethereal shell which, in the case of an isolated atom, has a spherical form; the atom itself is the carrier of the specific affinities, the surface of the shell is the seat of the valencies; each affinity is determined by the existence of two opposite electrical poles, which are situated at the end-points of a straight line small in comparison with the diameter of the ethereal shell. Such a system of two electric poles is called a double- or dipole. The four valencies of a carbon-atom would be represented by four such di-poles, the middle points of which are situated on the surface of the ethereal shell, but freely movable within it. The dipoles themselves can rotate freely round their middle point. The carbon-atom has a greater attraction for positive than for negative electricity, and the positive pole of a valency is slightly stronger than the negative pole.

This hypothesis would explain—Why the four valencies take up the position of a regular tetrahedron; why they can be diverted from this position; why the valencies of one and the same carbon-atom cannot combine together, whilst the valencies of different carbon-atoms can do so; why there are two kinds of single-binding, (1)

one stable, (2) and the other allowing free rotation; and lastly, why free rotation ceases in cases of double- or treble-binding.

F. S. K.

On Valency. By H. E. ARMSTRONG (*Phil. Mag.* [5], 25, 21—30). The author extends Helmholtz's theory that the valency of an atom corresponds with the number of charges of electricity with which it is associated (*Trans.*, 1881, 277) by supposing that "molecular" combinations are due to the same cause. As instances of substances which may be looked on as molecular compounds, the author quotes the tetralkyl-compounds of ammonium. The stability of the iodides of these bases in the presence of potassium hydroxide is such as is shown by no other iodide except those of carbon; they fully resemble in this respect methyl iodide and iodobenzene. Moreover, although the heat of neutralisation of tetramethylammonium hydroxide is equal to that of potash whilst that of methyl alcohol is small, in the latter case the combination is incomplete and in many cases the salt produced is insoluble and does not interact with water. In aniline, the basic properties, so far from being entirely dependent on the nitrogen-atom, are lessened and ultimately almost annulled by the introduction of halogens into the phenyl radicle. Some hydrazines are monobasic, others bibasic, although they all contain two (triad) nitrogen-atoms: hence, the pentad nature of the nitrogen in the salts of these substances is doubtful, and they are better considered as so-called molecular compounds. To explain these molecular combinations, the charge of electricity is supposed to penetrate the atom and to have varying degrees of freedom of motion. In some combinations, such as H_2 , the opposite charges approach one another, and there is no residual affinity; whilst in others, such as HCl , the charges of some of the atoms do not move towards those of their neighbours, their influence is not entirely neutralised and a residual affinity obtains. In tetramethylammonium iodide, the nitrogen of the molecule NMe_3 has such a residual affinity which is neutralised by a similar residual affinity in the iodine of the methyl iodide. Ammonium haloïd compounds, in that they can further combine with halogens, show residual affinity, but it is not probable that the halogen of the ammonium salt serves as the bond of union. On the other hand, in the double metallic salts the halogen does play this part, and from their analogy to ammonium haloïd compounds the halogen in the latter should serve as the bond of union. In view of this conflict of evidence, the theory of the ammonium radicle is questioned, and the perhalogen-compounds are regarded as formed by the union of the halogen with the nitrogen-atom—a view supported by the fact that ammonium sulphate combines with halogens. That the same result is obtained in whatever order the radicles are inserted in a tetralkylammonium-compound may be due to isomeric change at the moment of formation, and does not necessarily prove the atomic constitution of these compounds. In the case of phosphorus, the existence of the compound PF_5 does not prove its quin-
quivalence in face of the compounds H_2F_2 and $HFFR$, which prove that fluorine can combine with itself. Instead of the constitution $Cl_2P \cdot OCl$ for phosphorus oxychloride, the oxygen may be considered

to be united to the phosphorus-atom in PCl_3 by residual affinity. For bismuth, the compound BiPh_3Br_2 only proves that it belongs to the nitrogen-phosphorus-group so long as its constitution is unknown. In the compounds PbEt_4 and TeCl_4 the lead and tellurium atoms may be considered to have charges showing little mobility, hence each charge binds two monad atoms. The elements of the carbon-silicon-group are probably tetrads, whilst iron in the ferric compounds is a triad. Chlorides in which the chlorine-atoms form a closed chain are also conceivable. From the above it follows that, except in the paraffins, benzenes, and their haloïd and alcoholic derivatives, the constitution of compounds is by no means settled, and that a more liberal interpretation of facts than heretofore must be made. H. K. T.

Tetravalency of Oxygen. By J. F. HEYES (*Phil. Mag.* [5], 25, p. 221—237).—The author considers that molecular compounds of haloïd salts can be better explained by supposing the haloïds to be trivalent than by grouping the atoms round a central atom, which must, therefore, have a very high valency. This, with the occasional tetravalency of oxygen, gives formulæ for the oxychlorine acids more in accord with their properties than those in use. Thus potassic hypochlorite becomes $\text{K}-\text{Cl}=\text{O}=\text{O}=\text{Cl}-\text{K}$, whilst the substances KClO_3 , KClO_4 may be looked upon as $\text{K}-\text{Cl}=\text{O}$ united to groups of oxygen-atoms $(\text{O}_3)''$ or $(\text{O}_4)''$, forming perhaps a closed chain.

The tetravalence of oxygen is supported by the peroxides, BaO_2 , MnO_2 , whose properties, distinct from those of SnO_2 , SiO_2 , point to a composition $\text{X}''=\text{O}=\text{O}$, and by the oxides of silver, mercury, and copper. Sodium dioxide, since it is not decomposed by heat, is considered to have the structure $\text{Na}-\text{O}-\text{O}-\text{Na}$, whilst in K_2O_4 there is an (O_4) nucleus related probably to that in KClO_4 and Cl_2O_4 . The interaction of water with organic substances such as aldehyde, acetal and acetic acid, favours the view of the occasional tetravalency of oxygen, as do also the gaseous acetic acid molecule ($\text{C}_4\text{H}_8\text{O}_4$) of Ramsay and Young, and Friedel's substance, $(\text{CH}_3)_2\text{O}, \text{HCl}$. The double metallic oxides, basic salts, and water of crystallisation ($-\text{OH}_2\cdot\text{OH}_2\cdot\text{OH}_2-$, &c.) also favour this view. In substances where there are two valencies the author proposes the term validity to indicate the less powerful affinity: thus chlorine is monovalent and trivalid; carbon is tetravalent, except in CO and CNO , where it is bivalid. J. J. Thomson has pointed out that according to the vortex theory a dyad might unite not only with two atoms but also with four atoms of a monad, so that water consists of three primaries $\text{H}_2-\text{O}-\text{O}$. The author's formula, $\text{H}_2=\text{O}=\text{O}$, agrees with this theory and also with Brodie's $\text{H}_2\ddot{\text{O}}\ddot{\text{O}}^+$. As an instance of a radicle at once mono- or tri-valent, the author quotes $(\text{C}_3\text{H}_5)'''$, which if regarded as an atom is analogous to gold or thallium. H. K. T.

Investigation of the Second van't Hoff Hypothesis. By K. AUWERS and V. MEYER (*Ber.*, 21, 784—817).—This vol., p. 597.

Simple Procedure for the Determination of Molecular Weights by Raoult's Method. By A. F. HOLLEMAN (Ber., 21, 860—862).—The simplifications introduced proceed on the same lines as those already described by V. Meyer and by K. Auwers (this vol., pp. 407—409).

Ancient Process for making Gems and Glasses Phosphorescent. By BERTHELOT (*Compt. rend.*, 106, 443—446).—An extract from ancient Greek MSS. containing recipes for making gems, glasses, &c., phosphorescent, or imparting to them more brilliant colours, by coating them with thin layers of various-coloured or phosphorescent substances, the latter being usually of the nature of readily oxidisable organic compounds.

C. H. B.

Inorganic Chemistry.

Rate at which Bleaching Powder loses its available Chlorine when kept at Different Temperatures. By J. PATTINSON (*J. Soc. Chem. Ind.*, 7, 188—191).—It is shown that although the available chlorine of bleaching powder disappears in proportion to the length of time it is kept and to the temperature to which it is subjected, yet, within a comparatively small amount, the whole of the chlorine it originally contained is still retained in some form or other in combination with the calcium of the compound. This, at any rate, is true of bleaching powder when kept in casks or bottles for about 12 months at temperatures varying from 15.5° to 26.5°. D. B.

Preparation of Tetrathionates from "Wackenroder's" Solution. By T. CURTIUS and F. HENKEL (*J. pr. Chem.* [2], 37, 137—149; compare Debus, *Trans.*, 1888, 278).—When "Wackenroder's" solution is shaken for a considerable time with excess of barium carbonate and then filtered, the solution is quite clear, neutral to litmus, and contains sulphur and barium present in the ratio of four atoms of the former to one of the latter, thus corresponding with barium tetrathionate. If, however, the solution is imperfectly neutralised it will contain acid tetrathionates, and consequently sulphur will be present in a quantity larger than that represented by the ratio $S_4:Ba$. The existence of these acid tetrathionates, unknown until now, has led many investigators to wrongly assert that polythionic acids, containing more sulphur than tetrathionic acid, are present in Wackenroder's solution. Pure barium tetrathionate may be obtained from Wackenroder's solution, which has been completely neutralised by barium carbonate, by precipitating with alcohol and then alternately dissolving in water and precipitating with absolute alcohol. As thus prepared, the salt is identical with that formed by the action of iodine on the thiosulphate, and has the formula $BaS_4O_6 + 2H_2O$.

If Wackenroder's solution is neutralised by means of the carbonates of zinc and manganese, and then an equal volume of the solution added, acid salts of these metals are obtained. These acid salts are much more stable than the normal ones, and dissolve readily in cold absolute alcohol, from which they can be recrystallised over sulphuric acid in a vacuum. The zinc salt, $(\text{S}_2\text{O}_6\text{H})_2\text{Zn}$, crystallises from alcohol in groups of small needles, is somewhat hygroscopic, and is exceedingly soluble in cold water and in cold alcohol. It decomposes at a little above 100° , and addition of potash to the aqueous solution causes an immediate separation of sulphur. The manganese salt, $(\text{S}_2\text{O}_6\text{H})_2\text{Mn}$, crystallises in rose-coloured plates, and in all its other properties much resembles the zinc salt. The authors have observed the peculiar appearance and properties of the sulphur present in Wackenroder's solution (Debus, *loc. cit.*). G. T. M.

Hydrofluorides of Potassium Fluoride. By H. MOISSAN (*Compt. rend.*, 106, 547—549).—When dry, powdered potassium fluoride is gradually added to liquid anhydrous hydrofluoric acid it dissolves rapidly with development of heat, and if the solution is cooled to -23° it yields highly hygroscopic crystals of the hydrofluoride of potassium fluoride, $\text{KF} \cdot 3\text{HF}$. This compound gives off hydrogen fluoride in moist air, and dissolves rapidly in water with liberation of acid and great reduction of temperature. When heated, it loses hydrogen fluoride and yields a residue of potassium fluoride. At 100° , the fused salt has no action on crystallised silicon, but if rapidly heated to a higher temperature the mixture becomes incandescent with violent evolution of silicon fluoride. The fused salt acts energetically on silica and decomposes carbonates. It is decomposed by sulphuric acid in the cold with very rapid evolution of hydrogen fluoride, and acts energetically on potash and ammonia.

If the potassium fluoride and hydrogen fluoride are mixed in suitable proportions, the compound $\text{KF} \cdot 2\text{HF}$ is obtained; this is liquid at 105° , and on cooling forms crystals similar to those of the preceding compound. It may be kept liquid between 65° and 105° , and under these conditions acts readily on many minerals and organic substances.

These compounds are analogous to Berthelot's hydrochlorides of chlorides and Troost's compounds of ammonia with ammonium salts. The trihydrofluoride is, however, somewhat stable, and decomposes very slowly in dry air or even in a vacuum. C. H. B.

Preparation of Cakes of Ammonium Chloride and Ammonium Carbonate. By W. HEMPEL (*Ber.*, 21, 897).—When heated at 50 — 100° and subjected to hydraulic pressure, powdered ammonium chloride and ammonium carbonate are respectively converted into hard cakes. W. P. W.

Soluble Phosphates in Superphosphates. By H. OTTO (*Chem. Centr.*, 1887, 1563—1564; from *Zeit. Chem. Ind.*, 2, 207—210).—The solubility of the pure calcium salt, $\text{CaH}_2(\text{PO}_4)_2$, in water at 15° is about 1 in 25. Solutions of the phosphate do not undergo decomposi-

tion at the ordinary temperature; at 50° , slight decomposition begins, and at 90° CaHPO_4 is precipitated, free phosphoric acid going into solution.

Acid phosphate of iron, $\text{FeH}_6(\text{PO}_4)_3$, is decomposed by water at the ordinary temperature into FePO_4 and free phosphoric acid; the greater the volume of water, the more complete the decomposition. Acid phosphate of aluminium on the other hand does not decompose, but dries to a white, colourless mass, again soluble in water. It decomposes on heating. Acid phosphate of manganese, which occurs in some superphosphates, forms a bright rose-coloured, crystalline product, which is easily soluble in water, and is not decomposed even by large quantities of water.

The whole of the soluble phosphates of aluminium and manganese existing in superphosphate are dissolved in estimating the soluble phosphates.

In consequence of the decomposition which acid phosphate of iron undergoes, and the partial decomposition between the iron and monocalcic phosphates, the soluble phosphate obtained by the process recommended by the Magdeburg Conference (namely, extraction with a large volume of water at once, 1,000 c.c. to 20 grams superphosphate) is considerably less than that obtained by the usual process of extracting with successive small quantities.

A comparison of the two methods with a superphosphate containing 49.9 per cent. P_2O_5 , gave the following result: Magdeburg method, 45.8 per cent. P_2O_5 ; usual method, 47.2 per cent. P_2O_5 .

J. P. L.

Anhydrous Magnesium Chloride. By W. HEMPEL (*Ber.*, **21**, 897).—Crystallised magnesium chloride can be rendered anhydrous and the formation of basic salt prevented by heating it in a current of hydrogen chloride.

W. P. W.

Instability of the Double Sulphates, $\text{M}''\text{SO}_4, \text{R}'_2\text{SO}_4 + 6\text{H}_2\text{O}$, of the Magnesium Series. By W. DITTMAR (*Proc. Roy. Soc. Edin.*, **124**, 219—220).—When to a solution of a known weight of potassium sulphate, dissolved in a quantity of hot water less than sufficient to hold the intended double salt in solution, a known weight of the bivalent sulphate amounting to exactly 1 or 1.1, 1.2—1.5MgO, or FeO per $1\text{K}_2\text{O}$, is added, the resulting crystals are found to be coated with potassium sulphate; with 1.2 or 1.3MgO per $1\text{K}_2\text{O}$, the crystals become more and more pure. The results with ferrous sulphate are similar.

E. W. P.

Action of Potable Water on Lead Pipes. By E. REICHARDT (*Arch. Pharm.* [3], **25**, 1049—1052; compare this vol., p. 344).—Present experience shows that waters which act on lead pipes, generally, if not exclusively, contain free carbonic anhydride. The view that lead pipes gradually become coated internally so as to resist this action is still wanting proof. It has been ascertained that the addition of finely-powdered calcium carbonate suffices perfectly to prevent the action; the free carbonic anhydride quickly attacks the carbonate, leaving any excess undissolved.

J. T.

Corrosion of Lead Water Pipes. By T. CARNELLEY and W. FREW (*J. Soc. Chem. Ind.*, 7, 15—20, and 78).—The results show that the corrosion is much greater with free exposure to the air than by exclusion of the latter; the action of water being diminished to about one-fourth, and that of calcium hydroxide to about one-fifth, when air is excluded. This confirms the observations of previous investigators. The most important result, however, is the great protective action exerted by sand, calcium carbonate, old mortar, calcium silicate, and a mixture of sand and calcium carbonate. The circumstance that the presence of sand has a most important effect in protecting lead from corrosion has already been shown by Crookes, Odling, and Tidy, in a report on the action of water on lead made to the Water Committee of the Corporation of Huddersfield in 1886. In this report, it is shown that the action of soft water on lead is regulated by the amount of silica contained in the water, and also that the most effectual way to silicate a water is to pass it over a mixture of flints and limestone. They do not, however, give any reason or experiment to show why a mixture of these two should be more effectual than either alone. The authors are of opinion that the true explanation is to be found in the formation of calcium silicate, and as a proof assign the fact that calcium silicate itself, either as such or in the form of old mortar, is more effective than either calcium carbonate or silica separately (compare Müller, this vol., p. 225, Reichardt, p. 344, and preceding Abstract). D. B

Displacement of Copper by Zinc. By A. DESTREM (*Compt. rend.*, 106, 489—492).—Pure zinc introduced into solutions of copper salts with strong acids produces a brown or blackish slightly adherent deposit of copper. In slightly alkaline solutions, the deposit is red and firmly adherent. In the case of copper salts of feeble acids the deposit has the colour of brass and is strongly adherent, especially if the solution is electrolysed for a short time with an anode of metallic copper.

Pure carefully cleaned zinc was immersed for brief equal intervals of time in solutions of cuprammonium sulphate, cupric acetate, cupric formate, and cupric picrate. At first the weight of the zinc increases, but afterwards it gradually diminishes with each successive immersion and tends to become constant. If there were simply an exchange of copper for zinc, the weight of the zinc should always decrease. The yellow colour of the deposit, its firm adherence to the zinc, and the increase in weight indicate that on the first immersion of the zinc into neutral or feebly alkaline solutions, alloys of zinc and copper resembling brass are formed. If the yellow deposit is touched with a rod moistened with hydrochloric acid, the red colour of copper appears, owing to the more rapid dissolution of the zinc. When the solution of the copper salt is acid, there is no increase in the weight of the zinc.

Similar phenomena are observed in the case of cadmium.

C. H. B.

Action of Sulphur Vapour on Copper. By H. N. WARREN (*Chem. News*, 57, 95).—If sulphur is thrown on to molten copper and

the mass allowed to cool when the reaction has ceased, a button is produced consisting of a core of pure copper enclosed in a uniform shell of copper sulphide; the thickness varying with the quantity of sulphur employed. In a similar manner, a rod of copper 1 inch in width was exposed at a dull red heat for half an hour to the action of sulphur vapour, in this case also, a layer of copper sulphide of uniform thickness was formed, leaving a core of pure copper. Good commercial copper must be used.

D. A. L.

Absorption of Carbonic Oxide by Cuprous Chloride. By W. HEMPEL (*Ber.*, **21**, 898—900).—Cuprous chloride solution absorbs noteworthy quantities of all gases, and it is therefore necessary to saturate a fresh solution with those gases in a mixture with which it does not enter into combination, otherwise the diminution in volume is greater than that due to the absorption of carbonic oxide; the results of the first analysis in which this solution is employed should consequently be rejected. When once saturated, the cuprous chloride solution gives very concordant results with gaseous mixtures whose composition is tolerably constant as, for example, with coal-gas. If, however, a solution, which has been used with one kind of gas, is employed for the analysis of a mixture of different composition, errors come in owing to the evolution of a portion of those dissolved gases which are absent from or are present in smaller proportions in the new mixture, and to the absorption of others; it is on this account that Drehschmidt found that the volume of the hydrogen increased in his experiments (this vol., p. 88; *Ber.*, **20**, 2753).

W. P. W.

Basic Aluminium Sulphate. By C. BOTTINGER (*Annalen*, **244**, 224—227).—A basic aluminium sulphate of the composition $\text{Al}_2\text{O}_3, \text{SO}_3, 6\text{H}_2\text{O}$, is deposited when a solution containing 5 grams of aluminium sulphate and $1\frac{1}{2}$ grams of common salt is heated at 140° in sealed tubes. It is insoluble in water, and loses 2 mols. H_2O at a dull red heat.

W. C. W.

Preparation of Potassium Manganate. By A. JOLLER (*Arch. Pharm.* [3], **25**, 970; from *Rep. anal. Chem.*, 1887, No. 33).—Potassium hydroxide (2 mols.) is placed in a crucible, some water is added, and finely divided potassium permanganate (2 mols.) is gradually added with constant stirring and heating. After two hours at a faint red heat, the crucible is cooled, and the manganate placed in a well-stoppered flask to prevent access of air and contact with organic matter.

The value of manganate as a reagent depends on its solubility in alkalis without change. The alkaline solution has the greatest tendency to produce with certain oxides precipitates which settle rapidly, and are constant in composition. Again, the solution is so powerful an oxidising agent that certain compounds are readily and perfectly oxidised at ordinary temperatures, whilst permanganate frequently requires heat and a large excess of reagent. Lastly, the end of the reaction is sharply defined, the green colour disappears, and the solution becomes colourless.

J. T.

Combination of Carbon with Iron under Pressure. By W. HEMPEL (*Ber.*, 21, 903).—When tested for its tensile strength, steel is found to give a fracture which is grey in the centre and brighter in colour towards the edge, whilst a fracture of the same specimen obtained in the ordinary way without extension has a uniform appearance. Inasmuch as contraction occurs in the former case previous to fracture, the author considers that owing to the resulting pressure a portion of the carbon present passes into the combined form (compare Spring and van't Hoff, this vol., p. 341), and ascribes the increase in the hardness of iron which occurs in wire-drawing or when it is hammered cold to a similar cause.

W. P. W.

Cobaltic Alums. By H. MARSHALL (*Proc. Roy. Soc. Edin.*, 123, 203—204).—When mixed solutions of cobalt sulphate and ammonium or potassium sulphate are electrolysed in a divided cell so arranged that the two electrodes are practically in separate vessels, the solution changes to greenish-blue, due to the oxidation of the cobaltous to a cobaltic compound. After crystallisation, a blue ammonium alum is obtained, which when dry is stable, but in solution rapidly becomes reduced, the oxygen which is liberated being in part ozone. A potassium alum was obtained but with less ease, but the salt was always mixed with potassium sulphate from which it could not be freed. Nickel salts of a corresponding composition have not hitherto been obtained.

E. W. P.

New Hydrate of Molybdic Acid. By A. VIVIER (*Compt. rend.*, 106, 601—602).—White crystals of the composition H_2MoO_4 , separated from a solution of ammonium molybdate in nitric acid. They may also be obtained by heating the ordinary molybdate solution at 50—60° with its own volume of water for several days.

C. H. B.

Titanium Chloride and Titanic Acid. By R. WAGNER (*Ber.*, 21, 960—962).—Commercial titanium chloride has always a yellowish or greenish colour; the former is usually due to ferric chloride, the latter to chlorine and sometimes to certain decomposition products of titanium chloride. A little stannic chloride was found in one sample, but with this exception, no foreign element other than iron could be detected. Chlorine, hydrochloric acid, and ferric chloride can be removed by slow distillation over sodium, other impurities are eliminated by fractional distillation.

A clear solution of orthotitanic acid can be obtained by adding water, in small quantities at a time, to titanium chloride, the mixture being well shaken during the process.

The hydrate of orthotitanic acid, precipitated in the cold from a clear solution in hydrochloric or sulphuric acid, yields, when dried in the air or at a moderate temperature, not only a white but also a green, brown, or black hydrate according to the treatment adopted; the latter is the final product of the orthohydrate.

When moist orthotitanic acid is heated, a remarkable play of colours is observed, and the oxide on further careful heating becomes almost white, but appears citron-yellow while hot; by continued

heating, the colour becomes more and more brownish. Metatitanic acid becomes brownish-coloured when ignited for a quarter of an hour.

If orthotitanic acid is allowed to remain under water for a long time it is partially converted into metatitanic hydrate.

The colour of titanium dioxide depends on the treatment to which it has been subjected. F. S. K.

Action of Vanadic Anhydride on Alkaline Fluorides. By A. DITTE (*Compt. rend.*, **106**, 270—272).—Sodium fluoride when heated in a closed crucible with an excess of vanadic anhydride yields a crystalline, red mass, and when this is treated with tepid water, it yields an orange solution, which deposits orange-red crystals of the composition $3V_2O_5, 4NaF + 18H_2O$. The mother-liquor when concentrated yields lemon-yellow crystals of the compound $V_2O_5, 4NaF$. With an excess of the alkaline fluoride, the product is pale-yellow, and is only slowly attacked by water. If extracted with warm water and the solution evaporated in a vacuum, the compound $3V_2O_5, 4NaF + 18H_2O$ is obtained in transparent, orange-red crystals, and the mother-liquor yields small, yellowish-white crystals of the compound $V_2O_5, 8NaF + 3H_2O$.

If a boiling saturated solution of sodium fluoride is mixed with excess of soluble vanadic anhydride and filtered, the filtrate deposits brilliant red crystals of the compound $V_2O_5, NaF + 5H_2O$, and the mother-liquor yields brilliant, lemon-yellow crystals of the compound $V_2O_5, 6NaF + 5H_2O$. All these sodium compounds are analogous to those previously obtained with potassium fluoride.

A warm concentrated solution of ammonium fluoride dissolves a large quantity of soluble vanadic anhydride, and the warm liquid deposits the compound $V_2O_5, 4NH_4F + 4H_2O$ in pale-yellow crystals, very soluble in water. When heated, they lose water and hydrogen fluoride, and yield the compound $V_2O_5, 2NH_4F$. If the mother-liquor from the first crystals is mixed with excess of vanadic anhydride, filtered and cooled, it deposits the compound $V_2O_5, 4NH_4F + 4H_2O$ in almost white, brilliant, nacreous needles, readily soluble in cold water. With a cold solution of ammonium fluoride and excess of vanadic anhydride, the first product consists of indistinct yellow crystals of the composition $V_2O_5, 8NH_4F + 4H_2O$, followed by crystals of the compound $V_2O_5, 4NH_4F + 4H_2O$.

Vanadic anhydride reacts with many other metallic fluorides, and the products are under investigation. C. H. B.

Action of Hydrogen Chloride on Cupric Chloride. By ENGEL (*Compt. rend.*, **106**, 273—275).—Hydrochloric acid precipitates cupric chloride from its solution in accordance with the author's law—that is to say, the sum of the equivalents of acid and salt in solution remains practically constant. At first the sum of the equivalents slightly diminishes, but when 10 c.c. of the solution contains 70 equivalents of hydrogen chloride the law is exactly obeyed. Beyond this point, the sum of the equivalents increases slowly as the proportion of free acid increases.

If a solution of cupric chloride is saturated with hydrogen chloride at 20–25° and then cooled to 0°, it deposits a hydrochloride of cupric chloride, $\text{CuCl}_2 \cdot \text{HCl} + 3\text{H}_2\text{O}$, in deep, garnet-red needles which lose hydrogen chloride and become green when exposed to air. Decomposition soon ceases in a closed vessel, and the crystals remain unaltered in an atmosphere of hydrogen chloride.

Dihydrated cupric chloride, $\text{CuCl}_2 + 2\text{H}_2\text{O}$, absorbs hydrogen chloride and becomes garnet-red, water being liberated. This fact, together with the colour of the hydrochloride, seems to indicate that the water is combined with the hydrogen chloride, and the cupric chloride is present in the anhydrous condition. The brown colour of a solution of cupric chloride containing much free hydrochloric acid is probably due to the presence of the hydrochloride.

It is noteworthy that all hydrochlorides of chlorides hitherto described contain water of crystallisation. C. H. B.

Preparation of Auroso-auric Chloride. By J. THOMSEN (*J. pr. Chem.* [2], **37**, 105–108).—Krüss and Schmidt have recently (this vol., p. 28) denied the existence of auroso-auric chloride, Au_2Cl_4 . The failure of their attempts to obtain it is considered to be due to the necessary temperature not having been maintained. Definite directions are now given for its successful preparation. By leading a stream of dry chlorine for 30 minutes over gold, precipitated from a solution of gold chloride by sulphurous acid, 50 to 70 grams of gold may be converted into a homogeneous mass corresponding with the formula Au_2Cl_4 . The reaction is started by gentle heating, but the necessary temperature is then maintained by the heat evolved in the reaction, provided that cooling is prevented by surrounding the tube with cotton or glass-wool. G. T. M.

Ruthenium Peroxide. By H. DEBRAY and A. JOLY (*Compt. rend.*, **106**, 328–333).—The instability of ruthenium peroxide prepared by the ordinary method is due to the presence of a small quantity of water. In order to obtain the oxide in a perfectly anhydrous condition it is enclosed in a tube which is contracted at the middle, one-half being filled with fused calcium chloride. When the tube is made vacuous, the ruthenium peroxide gradually sublimes, and that part of the tube which contains it is separated from the remainder by fusion and the oxide redistilled in a vacuum. The tubes in which it is preserved should be carefully cleansed from organic matter, and then dried by heating to redness whilst a current of hydrogen is passed through them.

Ruthenium peroxide melts at 25·5°, forming a deep orange-red liquid which solidifies slowly even in presence of crystals of the substance. The fused oxide remains vitreous for a long time, and can only be obtained in distinct crystals by sublimation, which takes place readily with very slight change of temperature under a pressure of 3 to 4 mm. It does not boil below 106°, and at 106–107° it decomposes. No ebullition was observed under any conditions. The vapour-tension is 183 mm. at 100·8°; 20 mm. at 42°, and practically *nil* at 0°. It may be distilled in water vapour if the latter contains chlorine or

hypochlorous acid; vapour-density by Dumas' method at 100° under a pressure of 106 mm. = 5.77; calculated for Ru = 104, 5.81. The peroxide attacks mercury, and acts slightly on glass in diffused light.

Ruthenium peroxide dissolves in water, forming a golden-yellow solution which contains no definite hydrates. The pure solution may be kept for some time, even in diffused light, but gradually decomposes with evolution of oxygen and deposition of a black layer of the oxide, Ru_2O_3 , which when dried above 100° contains 2 mols. H_2O . The exact amount of water, however, depends on the conditions of drying. The decomposition by water is more rapid the higher the temperature, and at 100° it rapidly becomes complete—brilliant black scales of the lower oxide, $\text{Ru}_4\text{O}_9, 2\text{H}_2\text{O}$, being obtained. This oxide becomes anhydrous at 360° without loss of oxygen, but at 440° it is converted into the dioxide. The oxide, Ru_4O_9 , is also obtained by heating the oxide, $\text{Ru}_2\text{O}_3, 2\text{H}_2\text{O}$, in a dry vacuum at a temperature not exceeding 360° .

The peroxide is stable below 106° , but at 107° sudden decomposition takes place with production of a smoky flame, the liquid portion being converted into the crystallised dioxide, whilst a pulverulent form of the same oxide is deposited on the sides of the tube. Decomposition is complete, but there is no actual explosion.

It has previously been shown (this vol., p. 426) that the peroxide is formed by the oxidation of the dioxide at 1000° , and it is evident that the relation between the dioxide and peroxide is similar to that existing between water and hydrogen peroxide.

C. H. B.

Mineralogical Chemistry.

Gold, Alunite, and Sulphur from New South Wales, and Native Antimony from Queensland. By R. W. E. MACIVOR (*Chem. News*, 57, 64).—Gold occurs at Gumdagai, in New South Wales, in fine flakes irregularly distributed through a matrix of serpentine, and varying in quantity from a few pennyweights to several ounces per ton. The serpentine is associated with an abundance of asbestos, and appreciable quantities of gold have also been found in some specimens of the latter mineral. Sulphur and alunite, yielding its own weight of alum perfectly free from iron, have been found in considerable quantities in Gloucester Co., N.S.W. The alunite is generally quite white, but sometimes has a very slight pinkish hue, probably due to a trace of manganese.

The author has examined some very pure specimens of antimony from Northern Queensland; all seemed to be water-worn, and some consisted of the metal only, others of the metal associated either with calcium carbonate or quartz.

D. A. L.

Stromeyerite from Zacatecas in Mexico. By G. A. KÖNIG (*Jahrb. f. Min.*, 1888, i, Ref., 190, from *Proc. Acad. Nat. Sci. Phila-*

delphia, 1886, 281).—The specimen analysed consisted of long, prismatic crystals, with broken ends, planted on quartz. The mineral has no cleavage; its colour is iron-grey, its hardness 3·5, and its sp. gr. 6·23. Analysis gave the following results:—

S.	Cu.	Ag.	Insoluble.	Total.
15·81	33·69	50·18	0·26	99·94

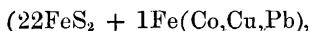
which corresponded with the formula CuAgS .

B. H. B.

New Mineral in the St. Bernard Lode at Hausach. By F. V. SANDBERGER (*Chem. Centr.*, 1887, 1568—1569, from *Öst. Zeit.*, **35**, 528—533).—The new mineral, which the author names *Metalonchidite*, consists of rhombic crystals like radiating pyrites, but distorted in the macrodiagonal axis, with irregular fracture, and hardness = 7; sp. gr. = 5·08. They are of zinc-white colour, and metallic lustre, and give on analysis—

S.	As.	Fe.	Ni.	Cu.	Pb.	Ag.	Total.
49·56	2·73	45·12	1·29	0·72	1·12	0·11	100·551

If the mineral is regarded as an isomorphous mixture of FeS_2 with FeAs_2 , the following formula, $25\text{FeS}_2 + 1\text{Fe}(\text{Ni}, \text{Cu}, \text{Pb}, \text{Ag})\text{As}_2$, which nearly approaches the formula of the lonchidite,



is obtained. The occurrence of silver and traces of gold and platinum in metalonchidite is worthy of notice.

J. P. L.

Association of Fluorspar with Babel Quartz at Ville-Vieille, near Pont Gibaud. By F. GONNARD (*Compt. rend.*, **106**, 558—560).—The lead mines at Ville-Vieille yield crystals of fluorspar with crystals of quartz embedded in their surfaces. These quartz crystals are arranged more or less regularly *en échelon*, just as in many English specimens. The author considers that the mode of occurrence indicates that the crystallisation of the quartz was simultaneous with that of the fluorspar, and not subsequent to it. Similar relations were observed to exist between crystals of quartz and crystals of chalcopyrites from Weardale.

C. H. B.

Caracolite and Percylite. By M. WEBSKY (*Jahrb. f. Min.*, 1888, i, Ref., 202—203, from *Akad. Wiss. Berlin*, 1886).—At Carocoles, in Chili, the rare mineral, percylite, occurs in small, azure-blue cubes in association with colourless crystals of caracolite. The composition of percylite is expressed by the formula $\text{Pb}_2\text{OCl} + \text{Cu}_2\text{OCl} + x\text{H}_2\text{O}$, that of caracolite by the formula $\text{HPbOCl} + \text{Na}_2\text{SO}_4$. The sp. gr. of caracolite is approximately 5·1. The crystals, which appear as though hexagonal, belong really to the rhombic system. The axial ratio is 0·5843 : 1 : 0·4213. (Compare Sandberger, *Abstr.*, 1887, 902.)

B. H. B.

Artificial Rubies. By E. FREMY and A. VERNEUIL (*Compt. rend.*, **106**, 565—567).—The rubies were obtained in the usual way by the

action of barium fluoride on alumina mixed with traces of potassium dichromate. The regularity of crystallisation depends on the proper regulation of the temperature. The product is a porous, friable mass, filled with geodes containing the rubies, which are separated by levigation. The rubies form transparent, regular, rhombohedral crystals of a red colour, which become dark on heating, but lighter again on cooling, like the natural gem. They are as hard as natural rubies, and scratch topaz.

C. H. B.

Mineralising Action of Alkaline Sulphides: Formation of Cymophane. By P. HAUTEFEUILLE and A. PERREY (*Compt. rend.*, **106**, 487—489).—Alkaline sulphides fused in a carbon crucible dissolve alumina at a dull red heat, and at higher temperatures crystals of corundum are obtained. The presence of an alkaline carbonate retards the mineralising action, and a greater proportion of the alumina forms soluble compounds.

Beryllia likewise dissolves in fused alkaline sulphides, and is converted into crystals, the proportion converted into soluble compounds being less than in the case of alumina, and independent of the presence or absence of alkaline carbonates. The crystals of beryllia thus obtained are colourless, transparent, and uniaxial, with positive compensation. The common form is a hexagonal pyramid, modified by faces on the edges of one of the bases, but the exact form depends on the temperature, and also on the presence or absence of alkaline carbonates.

A mixture of alumina and beryllia when dissolved in fused alkaline sulphides yields crystals with all the physical and chemical characteristics of cymophane. They are colourless and slightly opalescent, rhombic plates with a brilliant, adamantine lustre. Good results are obtained with a mixture of 100 parts of alumina, 40 parts of beryllia, 650 parts of potassium sulphate, and 150 of carbon. The product is treated with acidified water, and the uncombined beryllia is removed by treatment with warm, dilute, sulphuric acid and the carbon by calcination. Cymophane is always obtained, even in presence of a large excess of alumina and a very small quantity of beryllia. If an excess of beryllia is present, it becomes crystalline. Alkaline carbonates reduce the yield of cymophane and increase the proportion of crystallised beryllia.

C. H. B.

Jacobsite from the Sjö Mine. By L. J. IJELSTRÖM (*Jahrb. f. Min.*, 1888, i, Ref., 184, from *Bull. soc. franç. min.*, **10**, 170—174).—In the Sjö mine, Örebro, Sweden, microscopic crystals of jacobsite are found in calcite in the veins of hausmannite, associated with scheelite, polyarsenite, pyrrhoarsenite, tephrite, and iron glance. This jacobsite contains more mangauous oxide than the jacobsites of Langban and Jacobsberg. The best analyses gave the following results :—

	Mn ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	Total.
I.	18.42	51.54	30.04	100.00
II.	12.84	56.25	30.91	100.00

I after deducting 0·9 per cent. of tephrite; II after deducting 2·5 per cent. of tephrite and 4·9 per cent. of calcite. B. H. B.

Jacobsite from Nordmarken. By L. J. IGELSTRÖM (*Jahrb. f. Min.*, 1888, i, Ref., 184, from *Bull. soc. franç. min.*, **10**, 184—186).—Compact masses of jacobsite from Nordmarken in Sweden have the composition expressed by the formula $\text{Mn}_3\text{O}_4 + 2\text{Fe}_3\text{O}_4 + 6\text{MnO}, \text{Fe}_2\text{O}_3$, which is somewhat analogous to that of the franklinite of New Jersey. The percentages found by the author on analysis were—

Fe_2O_3 .	Mn_2O_3 .	MnO.
68·86	8·00	23·14

The percentage of ferrous oxide found is not stated.

B. H. B.

Two Varieties of Goethite from Saône et Loire. By A. LACROIX (*Jahrb. f. Min.*, 1888, i, Ref., 182.—183, from *Bull. soc. franç. min.*, **8**, 41).—At Chizeuil the author has found chocolate-brown to yellow, fibrous goethite having the following composition:—

Fe_2O_3 .	H_2O .	Total.	Sp. gr.
87·0	13·0	100·0	4·32

This mineral the author classes as lepidocrocite. At Romanèche, small geodes of hæmatite are covered with a velvety, chestnut-brown layer resembling the goethite of Przibram. B. H. B.

Pseudomorphs after Marcasite. By E. COHEN (*Jahrb. f. Min.*, 1888, i, Ref., 174—175, from *Situngsber. nat. Vereins Neu-Vorpommern u. Rugen*).—The concretions of marcasite, usually unaltered, in the chalk of Rügen are at Arkona altered, and form a brownish-yellow substance resembling yellow ochre. Usually all the marcasite has disappeared, and the concretion forms a pseudomorph, in the interior of which the radial structure of the marcasite may be detected. Analysis gave the following results:—

SiO_2 .	SO_3 .	Fe_2O_3 .	H_2O .	Loss on ignition.	Total.
9·30	4·30	66·80	6·70	13·72	100·82

The substance thus appears to be a mixture of 9·88 silica, 11·93 copiapite, and 78·19 limonite. B. H. B.

Occurrence of Epsomite on White Island, New Zealand. By R. W. E. MACIVOR (*Chem. News*, **57**, 114; compare this vol., p. 427).—Epsomite, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, is met with in many places as an efflorescence on the gypsum-covered floor of the crater. It contains a distinct trace of ferrous sulphate. D. A. L.

Mineralogical Notes. By F. A. GENTH (*Jahrb. f. Min.*, 1888, i, Ref., 187—188, from *Proc. Amer. Phil. Soc.*, **24**, 23).—1. *Mimetesite pseudomorphous after Anglesite*.—These crystals occur with the reni-

form tinstone of Durango, Mexico, and exhibit the combination P_{∞} , $\frac{1}{2}P_{\infty}$. Analysis gave the following results:—

As_2O_5 .	P_2O_5 .	PbO.	CaO.	Cl.	Ignition.
24.97	0.05	71.40	0.57	7.47	0.37

Together with 0.65 per cent. of clay and tin oxide.

2. *Vanadinite*.—Analyses are given of vanadinite from, I, Pinal Co., Arizona (brown); II, Pinal Co. (orange); III, Yavapai Co., Arizona (olive-green).

	V_2O_5 .	As_2O_5 .	P_2O_5 .	PbO.	CuO.	Cl.	Fe_2O_3 .	Less O.	Total.
I.	16.98	3.06	0.29	77.49	—	2.41	0.48	0.55	100.16
II.	17.16	4.30	trace	77.47	—	2.46	—	0.56	100.83
III.	18.64	trace	0.72	77.96	0.18	2.69	0.04	0.61	99.62

3. *Cuprodesclowitzite*, from San Luis Potosi, Mexico, occurs as a radiated incrustation 1 to 10 mm. thick, of a yellowish-brown colour and resinous lustre. Sp. gr. 6.203. Analysis gave—

V_2O_5 .	As_2O_5 .	P_2O_5 .	PbO.	CuO.	ZnO.	H_2O .	Total.
19.99	3.63	0.13	54.52	6.58	12.70	2.62	100.17

These numbers are in accord with the formula of desclowitzite, $(PbCuZn)_2OH(VAsP)O_4$, and confirm the accuracy of the former analyses of this mineral by Rammelsberg and Penfield.

4. *Pseudomorphs of iron pyrites after magnetic pyrites*, from Sulphur Creek, Colusa Co., California. The occurrence of iron pyrites in small, hexagonal tablets, 1 mm. in diameter, with rough basal planes and smooth prism planes, is regarded as a pseudomorph after magnetic pyrites.

5. *Hessite* from the West Side Mine, Tombstone, Arizona, occurs in quartz with cerargyrite and grains of gold. Sp. gr. 8.359. Analysis gave—

Ag.	Pb.	Te.	Total.
62.87	0.28	37.34	100.49

6. *Tapalpite* from the Sierra de Tapalpa, Mexico. This rare mineral occurs with iron pyrites, galena, quartz. and silicates. From analyses of impure material, the formula $Ag_3Bi(TeS)_3$ is deduced. The sp. gr. of the pure mineral is 7.75.

7. *Allanite* from Statesville, North Carolina, occurs with zircon crystals. It is brown-black in colour, has a sp. gr. of 3.63, and gave on analysis the following results:—

			$Ce_2O_3 + Di_2O_3 +$				
SiO_2 .	Al_2O_3 .	Fe_2O_3 .	La_2O_3 .		$Y_2O_3 + Er_2O_3$.	FeO.	MnO.
31.68	17.33	7.05	18.99		1.12	10.11	1.03
	CaO.	MgO.	Na_2O .	H_2O .	Total.		
	10.78	0.54	0.21	1.46	100.30		

B. H. B.

Pyrrhoarsenite, a New Mineral from the Sjö Mine. By L. J. IGELSTRÖM (*Jahrb. f. Min.*, 1888, i, Ref., 184—185, from *Bull. soc. franç. min.*, 9, 218—220).—This mineral occurs with barytes, tephroite, calcite, and hausmannite in narrow veins in the Sjö Mine. Optically it resembles the berzeliite of Langban. Its hardness is 4. Analysis gave the following results:—

As ₂ O ₅ + Sb ₂ O ₅ .	MnO.	CaO.	MgO.	SiO ₂ .	H ₂ O.	Total.
58·06	17·96	18·68	3·58	1·02	0·85	100·15

The mineral is thus an antimony-bearing berzeliite rich in manganese, and having the formula (CaMnMg)₃(AsSb)₂O₈ (compare Abstr., 1887, 902). B. H. B.

Pleochroism of Biotite. By E. COHEN (*Jahrb. f. Min.*, 1888, i, Mem., 165—169).—In cordierite and in muscovite, it is easy to prove by heating that the pleochroic borders first described by Rosenbusch are due to organic matter. In biotite, however, this phenomenon can only be explained with difficulty, heating with a Bunsen burner giving a negative result. This fact has induced Michel-Lévy and others to conclude that the pleochroic portions of biotite are due, not to organic matter, but to a concentration of ferriferous mica molecules. In biotite of the granite-porphyrries and gneisses of Urbies in Lower Alsace, such pleochroic borders are extremely abundant, and a number of sections have been examined by the author. When a thin section that has been carefully cleaned with ether is treated with dilute hydrochloric acid at a gentle heat, a period will be reached in which the biotite becomes considerably lighter in colour, although the pleochroic border presents no change. Even when the biotite is completely bleached, as long as the structure and double refraction remain, the pleochroic border will be unchanged. The latter disappears only when the section is strongly heated and then treated with dilute hydrochloric acid until the transparency is recovered. These experiments show that the pleochroic borders in biotite are due to organic matter whose decomposition requires a higher temperature than that of muscovite or of cordierite. B. H. B.

Manganese-zinc-serpentine from Franklin, New Jersey. By G. A. KÖNIG (*Jahrb. f. Min.*, 1888, Ref. 189, from *Proc. Acad. Nat. Sci. Philadelphia*, 1886, 355).—The material analysed was a compact, dark-brown serpentine, which in thin section exhibited a few grains of franklinite and of garnet. The analytical results were as follows:—

SiO ₂ .	MgO.	MnO.	ZnO.	H ₂ O.	Franklinite.	Pyroxene.	Total.
41·70	29·24	6·91	3·10	14·04	4·15	1·05	100·16

B. H. B.

Chrysocolla from California. By E. JANNETAZ (*Jahrb. f. Min.*, 1888, i, Ref., 183—184, from *Bull. soc. franç. min.*, 9, 211—213).—A specimen of opal mixed with the hydrated copper silicate contained

13 per cent. of water. The mixture had the following percentage composition:—

SiO ₂ .	CuO.	H ₂ O.	Fe ₂ O ₃ .	CuCl.	CaCO ₃ .	Total.
49.1	30.4	18.0	1.2	0.9	0.5	100.1

In thin sections, the copper silicate appears in radiated fibres having the same optical character (negative) as a diopase cut perpendicular to its axis. Chrysocolla from Chili and from Siberia exhibit similar optical characters.

B. H. B.

Analysis of Chiestolite. By W. MÜLLER (*Jahrb. f. Min.*, 1888, i, Ref., 175—176).—The author gives the following analysis of 0.1447 gram of chiestolite from the Alexandovski mine at Nertschinsk:—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	Loss on ignition.	Total.
34.85	62.28	0.85	0.89	98.87

Very similar results are obtained on analysing the andalusite of Brazil.

B. H. B.

Sanidinites from São Miguel. By A. OSANN (*Jahrb. f. Min.*, 1888, i, Mem., 117—130).—The sanidinites examined form part of the series collected in the Azores by Reiss and Hartung. Their structure is holocrystalline-granular. There is no amorphous cementing material, and no trace of porphyritic structure. Among the constituents of the rock, sanidine predominates, then follows hornblende or sometimes augite. All the rest, including mica and quartz, are subordinate. The accessory minerals are sodalite, zircon, pyrrhite, lavenite, titaniferous iron ore, and apatite. The sanidine is colourless and glassy, and on analysis gave the following results:—

SiO ₂ .	Al ₂ O ₃ + Fe ₂ O ₃ .	CaO.	Na ₂ O.	K ₂ O.	Total.	Sp. gr.
65.74	20.26	0.25	6.63	6.14	99.02	2.57

With regard to their geological occurrence and their mineralogical composition, the sanidinites form well-characterised rocks. At the Laacher See, in the Rhone, at Vesuvius, and at São Miguel, they always occur in the form of loose blocks, and have never been found in place.

B. H. B.

Copper Ores containing Tourmaline from Tamaya in Chili; Geological Occurrence of Boron Minerals. By A. V. GRODDECK (*Chem. Centr.*, 1887, 1518—1519, from *Zeit. Geol. Ges.*, **39**, 237—266).—The tourmalines are of microscopic size (0.1 to 0.5, in exceptional cases 2 mm. long, 0.05 to 0.1 mm. broad). They occur in (1) copper sulphides (copper pyrites, purple copper ore, and copper glance), (2) in the oxidised copper ores at the outcrop of the lode, (3) in the lode minerals (calcite and quartz), (4) in the matrix. An analysis gave—

SiO ₂ .	Al ₂ O ₃ .	B ₂ O ₃ .	FeO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.
36.34	32.22	10.87	8.31	0.79	3.92	3.14	0.22	3.89
Total.			Sp. gr.					
99.70.			3.2.	Traces of fluorine.				

A calcite from the Murciélagos mine of an anthraconite colour proved to be mixed with copper glance and tourmaline. In round numbers, 22 per cent. of copper glance, 36 per cent. tourmaline, and 42 per cent. calcite.

From the spathose, quartzose, micaceous, and chloritic matrix, and partition rocks of the lode, the following were submitted to analysis:—

I. A white, clear rock, consisting of 92 per cent. potash mica (sericite), 3 per cent. calcite, and 5 per cent. of silica (opal?).

II. The pure mica of the foregoing rock, which, however, still contained some purple copper ore, chlorite, and opal (?)

III. A porphyritic rock, in the crystalline matrix of which quartz, orthoclase, plagioclase, and titanite iron were embedded.

IV. A rock similar in structure to No. III, the felspar and matrix of which are changed into a fine-grained aggregate of quartz, sericite, and carbonate.

V. A solid porphyritic rock, in the grey matrix of which plagioclase, magnetic iron ore, titanite iron, and hornblende are embedded.

VI. A decomposed porphyritic rock consisting essentially of quartz and mica minerals, but also containing some tourmaline.

	I.	II.	III.	IV.	V.	VI.
SiO ₂ ...	43·88	42·61	75·93	63·85	59·54	66·44
Al ₂ O ₃ ..	31·43	34·02	13·26	17·51	13·09	17·43
Fe ₂ O ₃ ..	3·57	3·87	1·47	1·94	4·74	2·10
FeO...	0·88	0·95	0·68	0·18	6·13	1·60
MnO ..	—	—	trace	trace	0·49	—
MgO ..	0·65	0·70	—	—	1·33	3·70
CaO ...	3·73	2·42	1·11	0·96	3·81	0·65
K ₂ O ...	10·35	11·20	3·19	4·77	3·86	4·76
Na ₂ O ..	2·01	2·18	3·13	0·25	5·88	0·99
H ₂ O ...	1·89	2·05	0·44	1·02	0·68	2·13
CO ₂ ...	1·17	—	0·51	8·41	0·18	0·10
Total ..	99·56	100·00	99·72	99·73	100·32	99·902

No. III contains traces of TiO₂; IV, 0·84 of copper pyrites; V, 0·59 P₂O₅; VI, traces of SnO₂ and P₂O₅.

Besides the rocks analysed, which may be perhaps regarded as dioritic porphyrites, gabbro was found under the Tamaya rocks, but pure diorite and syenite, which have been previously described, were absent. Tourmaline was absent from all the solid partition rocks, and they were free from boron. The mineral is limited to the lode, lode minerals, and matrix of the ore. The question of the formation of the lodes, whether by lateral secretion or by the rise of hot springs, the author leaves open, but he considers the question of their formation from the activity of fumaroles to be excluded.

A geological grouping of boron minerals is also given.

J. P. L.

The Basalts of Alsace. By G. LINCK (*Jahrb. f. Min.*, 1888, i, Ref., 235—236, from *Mith. Commission geol. Landesunters. Elsass-*

Lothringen, 7, 49—68).—In Alsace, basalt occurs only in two places—at Reichshofen in Lower Alsace, and at Reichenweier in Upper Alsace. The basalt from the former locality is a felspar-basalt (Analysis I), whilst the basalt of Reichenweier is a limburgite (Analysis II), similar to that occurring at Forst in the Palatinate.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	FeO + Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
I.	52·60	0·57	14·17	11·38	9·17	6·37	1·06	2·90	2·08	100·30
II.	42·30	1·51	12·74	10·60	13·01	12·74	0·94	2·65	2·54	99·03

B. H. B.

Quartz Conglomerate from Witwatersrand, Transvaal. By P. HOLLAND (*Chem. News*, 57, 76—77).—The Witwatersrand reefs consist mainly of loose quartz conglomerate varying in colour from light yellow to dark-reddish or purplish-brown. A specimen of the dark variety consisted of waterworn quartz pebbles and angular fragments of coarse-grained quartzose sandstone of various sizes, mixed with siliceous matrix material. Scales of mica were also detected, but there was no “visible gold.” The sample as received contained slightly more than 15 dwts. of gold per ton; whilst those portions of the specimen passing through a $\frac{1}{4}$ -inch mesh sieve (amounting to about half the original), contained about 1 oz. 3 dwts. of gold per ton, and had the following general composition:—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	TiO ₂ .	MnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.
85·72	4·27	6·18	0·12	0·03	0·01	trace	0·23	0·32
Organic matter.				Water.	Total.			
0·29				2·56	99·73			

The gold is found chiefly in the matrix material.

D. A. L.

Chloritoid-schist from Grossarl. By A. CATHREIN (*Jahrb. f. Min.*, 1888, i, Ref., 242, from *Tschermak's min. Mitth.*, 8, 331—337).—In the Grossarl valley, Salzburg, a schist occurs containing numerous dark-green groups of chloritoid crystals in a yellowish-white ground-mass. The latter consists of quartz, rutile, titanite, iron pyrites, and titaniferous iron ore. The pulverised rock was boiled in dilute sulphuric acid, all the chloritoid and ore together with some titanite and rutile passing into solution. The soluble part (I) and the insoluble (II) gave on analysis the following results:—

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	FeO.	CaO.	MgO.	H ₂ O.	Total.
I.	25·50	1·88	38·69	27·19	0·40	0·08	6·67	100·41
II.	92·82	6·93	—	—	0·76	—	—	100·51

Calculated from I, the formula of the chloritoid is approximately $\text{H}_2\text{FeAl}_2\text{SiO}_7$. The composition of the rock, calculated from I and II, is 63·98 per cent. of chloritoid, 30·16 of quartz, 4·03 of rutile and ore, and 1·83 of titanite. Thus the proportion of chloritoid is greater than in any chloritoid schists known elsewhere.

B. H. B.

Labrador-porphyrries of the Vosges. By A. OSANN (*Jahrb. f. Min.*, 1888, i, Ref., 237—239; from *Abhdl. geol. Specialkarte Elsass-Lothringen*, 3, pt. 2).—The so-called labrador-porphyrries occur in the Southern Vosges, near the Sulzer Belchen, within a highly contorted series of culm rocks. The rocks examined by the author were found in the vicinity of Gebweiler, Masmünster, the Rossberg, Seewen, and St. Amarin. They have a brown, green, or grey colour, and consist principally of plagioclase and augite. The plagioclase appears to be labradorite, its extinction being 5° to 8° on OP, and 19° to 24° on $\infty P\infty$. The results of an analysis of unaltered plagioclase from the brown porphyry of the Rimbachthal were as follows:—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	Na ₂ O ₃ .	K ₂ O.	Total.
54.09	28.98	0.94	9.13	5.19	1.19	99.52

From these results the author deduces the composition



The augite in the rock is found by analysis to have an intermediate place between the diopside-like augites in granite and the augites in diabase.

B. H. B.

Analysis of Shotley Bridge Spa Water. By H. PEILE (*J. Soc. Chem. Ind.*, 7, 14).—The water when first collected is perfectly clear, but has a slightly brown tinge. It has a strong, ferruginous taste, which it loses on standing, when the taste of common salt may be readily detected. The sp. gr. at 15.5° is 1.00197, the temperature at the well 10° , the air at the time of observation being 14° . The water has for many years been used by persons suffering from rheumatism and skin diseases. The analysis of the water in grams per litre, and the percentage composition of the solid residue dried at 180° (2.484 grams per litre) gave—

	BaCl ₂ .	NH ₄ Cl.	CaCl ₂ .	LiCl.	MgCl ₂ .	KCl.
Water	0.0569	0.0042	0.2632	0.0065	0.0437	0.0513
Residue ...	2.29	—	10.95	0.26	1.76	2.06

	NaCl.	CaH ₂ (CO ₃) ₂ .	CaCO ₃ .	MgH ₂ (CO ₃) ₂ .	FeH ₂ (CO ₃) ₂ .
Water	1.7333	0.3964	—	traces	0.155
Residue ...	69.77	—	11.08	—	—

	MnH ₂ (CO ₃) ₂ .	Fe ₂ O ₃ .	MgBr ₂ .	MgI ₂ .	MgCO ₃ .	SiO ₂ .
Water	traces	—	0.0075	0.000056	—	traces
Residue ...	—	0.62	0.30	0.002	traces	traces

	P ₂ O ₅ .	Mn.	Albuminoid NH ₃ .	Total CO ₂ .	Free CO ₂ .	Totals.
Water	traces	—	traces	0.3340	0.0833	—
Residue ...	traces	traces	—	—	—	99.092

D. B.

Chemical Composition of the Water composing the Clyde Sea Area. By A. DICKIE (*Proc. Roy. Soc. Edin.*, 124, 422—427).

Organic Chemistry.

Fire-damp. By B. FRANKE (*J. pr. Chem.* [2], **37**, 91--101, 113--136).—The author has made an elaborate series of experiments on the origin of fire-damp. Examination and analyses of many samples of gas taken from mines under different conditions show that they may be roughly classified, according to the nature of the gas contained in the coal, under the three following heads:—(1) Mines, the coal of which gives an incombustible gas consisting of much nitrogen and little methane. (2) Mines, the coal of which gives a combustible gas, not capable however of forming an explosive mixture with air. In such mines, the coal should be worked in ascending galleries and the efficiency of the ventilation occasionally checked by analysis of the air. (3) Mines, the coal of which gives gases rich in methane and forming explosive mixtures with air. In mines of this class, safety lamps must be used together with a perfect system of exhaust ventilation from every point at which coal is worked.

G. T. M.

Decomposition of Chloroform by Alcoholic Potash. By L. DE ST. MARTIN (*Compt. rend.*, **106**, 492—495).—A solution of potassium hydroxide in alcohol of 60° decomposes chloroform slowly but almost completely at the ordinary temperature, and decomposition is rapid at 100°. If the strength of the potash solution is known, the excess may be determined by titration, using phenolphthalein as indicator, and after the liquid has been carefully cooled the amount of the potassium chloride formed may be estimated by silver nitrate solution with potassium chromate as indicator. In the cold solution the alcohol and potassium formate have no effect on the titration. In order to employ this method for the estimation of chloroform, the latter is heated with the alcoholic potash in sealed tubes, and the excess of potash and amount of chloride formed are estimated.

In order to determine the quantity of chloroform vapour in air or other gases, a known volume of the gas is allowed to enter a vacuum globe into which a measured quantity of alcoholic potash is then introduced. After standing for eight or ten days an aliquot part of the potash solution is withdrawn and titrated.

C. H. B.

Purification of Chloroform. By H. WERNER (*Arch. Pharm.* [3], **25**, 1113—1115).—The method of purifying chloroform published by the author in 1878 (*Abstr.*, 1878, 821) affords a product found to be perfectly satisfactory for medicinal use during 10 years' experience, even if an isolated sample, may barely pass the phenolphthalein tests given by Vulpus (this vol., p. 634).

J. T.

Geuther's Views on the Constitution of the Nitro-derivatives of the Adipic Hydrocarbons. By V. MEYER (*Annalen*, **244**, 222—224).—A reply to Götting's remarks on the constitution of nitroethane (this vol., p. 355).

Ethyl Ferrocyanide. By M. FREUND (*Ber.*, **21**, 931—936).—When a carefully cooled alcoholic solution of hydroferrocyanic acid is saturated with dry hydrogen chloride, a compound, $C_{18}H_{42}N_6O_6FeCl_2$, is obtained (compare Buff, *Annalen*, **91**, 253), which crystallises in white needles, decomposes into its constituents on exposure to the air, and when heated becomes dark-blue, and at a higher temperature glows, leaving a pseudomorph of iron oxide. Alcoholic ammonia converts it into the ammonium salt, $(NH_4)_4FeC_6, 2NH_4Cl$. Contrary to Buff's statement, ethyl ferrocyanide is not formed when it is dissolved in hot alcohol and treated with ether, since the product is hydroferrocyanic acid, and on this account the compound is to be regarded as probably analogous in constitution to the imido-ethers, and may be represented by the formula $H_4FeC_6(OEt)_3(NH)_6, 2HCl$. The corresponding *methyl*-, *propyl*-, and *amyl*-derivatives were also prepared.

Ethyl ferrocyanide, Et_4FeC_6 , is obtained by boiling silver ferrocyanide with ethyl iodide for about an hour until the product begins to be coloured blue. It crystallises from chloroform by spontaneous evaporation in large, rhombic forms, decomposes at 212° — 214° with the formation of ethylcarbamine, and is readily soluble in water, alcohol, and chloroform, but insoluble in ether, light petroleum, and carbon bisulphide. In aqueous solution, it yields a deep-violet colour with ferric chloride, and a white precipitate with mercuric chloride. Concentrated sulphuric acid decomposes it with the formation of carbonic oxide and the sulphates of iron, ammonia, and ethylamine.

When finely powdered potassium ferricyanide, suspended in alcohol, is saturated with dry hydrogen chloride, a compound, $C_{18}H_{42}N_6O_6FeCl_2$ or $C_{18}H_{44}N_6O_6FeCl_2$, is obtained, which crystallises in needles, decomposes very readily, and in its other properties resembles the compound prepared from hydroferrocyanic acid.

W. P. W.

Ethyl Platinocyanide. By M. FREUND (*Ber.*, **21**, 937—938).—The compound obtained by v. Than (*Annalen*, **107**, 315), and by him termed ethyl platinocyanide, most probably has not this composition but is analogous in constitution to the imido-ethers. For example, when heated on a water-bath it is converted into hydrogen platinocyanide, when decomposed with water it yields hydrogen platinocyanide and alcohol, and on treatment with alcoholic ammonia it is converted into ammonium platinocyanide (compare preceding Abstract).

W. P. W.

Formation of a Glycol in the Alcoholic Fermentation of Sugar. By HENNINGER and SANSON (*Compt. rend.*, **106**, 208—209).—Sugar was mixed with yeast, and after 15 days tartaric acid was added. When fermentation ceased, the product was fractionated and the portion boiling between 175° and 182° was refractionated. In this way, isobutylene glycol boiling at 178 — 179° was obtained, the yield amounting to 3.08 grams per kilo. of sugar.

C. H. B.

Formose and Methylenitan. By O. LOEW (*J. pr. Chem.* [2], **37**, 203—206).—In this paper, the author contests the opinion advanced by Tollens (this vol., p. 438), that formose and methylenitan are identical. The reducing power of formose is nearly equal to that

of dextrose, it has a sweet taste, and if dried carefully, so as to prevent decomposition, gives on analysis numbers corresponding with the formula $C_6H_{12}O_5$. Methylenitan has, on the other hand, a bitter taste, a reducing power of only one-fifth to one-fourth of that of dextrose, does not yield an osazone, and is represented by the formula $C_6H_{10}O_5$.
G. T. M.

Alcoholic Fermentation of Galactose. By E. BOURQUELOT (*Compt. rend.*, **106**, 283—286).—Pure galactose is not fermented by either high or low beer yeast, but if the galactose is mixed with glucose and then with yeast it undergoes alcoholic fermentation. The limit of fermentation is the same whether the glucose and galactose are mixed in equal proportions, or the former is only one-thirtieth of the latter, but with the smaller proportion of glucose about thrice the time is required.

Levulose or maltose mixed with galactose and yeast have the same effect as glucose, and bring about the fermentation of the galactose.

C. H. B.

Compounds of Sugars with Aldehydes and Acetones. By H. SCHIFF (*Annalen*, **244**, 19—28).—The addition of a small quantity of aldehyde or acetone to a cold concentrated solution of glucose or cane-sugar in strong acetic acid, produces a gum-like deposit which adheres to the sides of the vessel. By washing the substance with glacial acetic acid, and afterwards treating it with absolute alcohol, it solidifies to a hygroscopic mass readily decomposed by water. These compounds contain sugar and aldehyde or acetone in equal molecular proportions. Dextrose forms compounds with benzaldehyde, salicylaldehyde, cumaldehyde, furfuraldehyde, acetaldehyde, ethyl acetoacetate, and camphor, and cane-sugar combines with cænanthaldehyde, furfuraldehyde, and camphor. Milk-sugar does not form similar compounds.
W. C. W.

Bases formed by Alcoholic Fermentation. By E. C. MORIN (*Compt. rend.*, **106**, 360—363).—A quantity of crude unwashed fusel oil boiling at 130 — 135° was agitated with dilute hydrochloric acid, and the separated acid solution distilled until the last traces of alcohol were expelled. It was then made alkaline and again distilled, when the bases passed over with the first portions of the distillate. The bases were dried over potash and separated into three fractions, boiling respectively at 155 — 160° , 171 — 172° , and 185 — 190° . Similar products were obtained from both washed and unwashed fusel oils, but the yield was smaller in the case of the former.

The base boiling at 171 — 172° has the composition of $C_7H_{10}N_2$. It is a mobile, colourless, highly refractive, almost neutral liquid with a strong disagreeable odour; sp. gr. = 0.9826 at 12° ; vapour-density 4.16 . When heated with hydrochloric acid, it is partially decomposed with formation of ammonium chloride, but no evidence as to its constitution is obtained. It combines with ethyl iodide, forming yellow needles which dissolve in water and alcohol but are insoluble in anhydrous ether. The *hydrochloride* crystallises in slender, white needles, soluble in water and ethyl alcohol, but only slightly soluble

in ether. The platinochloride is crystalline and very soluble in water and alcohol, but only slightly soluble in ether, although it dissolves in a mixture of ether and alcohol. It decomposes when the aqueous or alcoholic solution is evaporated in a vacuum.

Mercury potassium iodide gives no precipitate in aqueous solutions, but after the addition of a small quantity of hydrochloric acid it yields a yellow, flocculent precipitate which rapidly changes to characteristic brilliant, slender needles.

Pyridine and quinoline bases do not give this reaction. Mercuric chloride or phosphotungstic acid produces a flocculent, white precipitate; phosphomolybdic acid, a yellow precipitate. C. H. B.

Bases produced by Alcoholic Fermentation. By TANRET (*Compt. rend.*, 106, 418—419).—The base, $C_7H_{10}N_2$, obtained by Morin from the products of alcoholic fermentation (preceding Abstract) seems to be identical with the glucosine, $C_7H_{10}N_2$, obtained by the author by the action of ammonia on glucose (Abstr., 1885, 1048). C. H. B.

Amidothiazoles from Thiocarbamide and Halogenated Ketones and Aldehydes. By A. HANTZSCH and V. TRAUMANN (*Ber.*, 21, 938—941).—The authors find that not only does the reaction between halogenated ketones and thiocarbamide-derivatives take place more readily than with ammonium thiocyanate (this vol., p. 256), but the yield also is almost quantitative, and the products consist not of substituted thiocarbamides as Pawlewski states (this vol., p. 473), but of thiazole-derivatives. Thus, the product of the action of chloroacetone on thiocarbamide is not acetylthiocarbamide but mesoamido-methylthiazole. The term thiazoline is proposed for amidothiazole.

Thiazoline, $\langle \begin{smallmatrix} N:C(NH_2) \\ CH:CH-S \end{smallmatrix} \rangle$, is prepared from dichlorether, and phenylthiazoline from bromoacetophenone by the action of thiocarbamide. These strongly characterised bases resemble in their properties the bases of the aromatic series, and like these can be diazotised, forming diazothiazole salts, which react with aromatic amines and with phenols, yielding the corresponding amido- and hydroxy-azo-derivatives.

Mono-substituted thiocarbamides yield secondary thiazylamines by the action of halogenated ketones. Phenylamidothiazole or thiazylaniline, $\langle \begin{smallmatrix} N:C(NHPh) \\ CH:CH-S \end{smallmatrix} \rangle$, is obtained from phenylthiocarbamide and dichlorether.

The so-called sulphuvinuric acid, prepared by Nencki and Sieber (Abstr., 1882, 501) by the action of thiocarbamide on dibromopyruvic acid, is most probably amidothiazolecarboxylic acid, $\langle \begin{smallmatrix} C(NH_2):N \\ S-CH \end{smallmatrix} \rangle C \cdot COOH$.

W. P. W.

Methylthiazole. By A. HANTZSCH and L. ARAPIDES (*Ber.*, 21, 941—942).—The authors have obtained the free thiazoles. α -Methylthiazole, $\langle \begin{smallmatrix} N:CH-S \\ CMe:CH \end{smallmatrix} \rangle$, is formed when the hydroxy-derivative (this

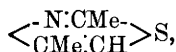
vol., p. 256) is distilled with zinc-dust. It resembles α -picoline in every respect, particularly in odour and boiling point.

When the reaction-product of dichlorether and barium thiocyanate is distilled with zinc-dust, small quantities of a compound with a strong pyridine smell are obtained; this substance is most probably *thiazole*.

F. S. K.

Synthesis of Thiazoles and Oxazoles. By A. HANTZSCH (*Ber.*, **21**, 942—946).—Thioamides condense with α -halogen-substituted ketones to form thiazoles.

Thioacetamide and chloracetone yield *xx-dimethylthiazole*,



a base which in smell, boiling point, &c., can scarcely be distinguished from *xx-lutidine*.

Phenylmethylthiazole, $\langle \begin{array}{c} \text{N}:\text{CMe}- \\ \text{CPh}:\text{CH} \end{array} \rangle \text{S}$, is formed by the condensation of thioacetamide with acetophenone bromide.

Methylthiazole, $\langle \begin{array}{c} \text{N}:\text{CMe}- \\ \text{CH}:\text{CH} \end{array} \rangle \text{S}$, is produced, but only in small quantities, by the condensation of dichlorether with thioacetamide. *Oxazoles* are obtained by the condensation of α -halogen-ketones with amides; the compounds obtained by Lewy (this vol., p. 556) from acetophenone bromide and acetamide, and also the other compounds which he produced in a similar manner, are doubtless derivatives of oxazole, $\langle \begin{array}{c} \text{N}:\text{CH}\cdot\text{O} \\ \text{CH}:\text{CH} \end{array} \rangle$.

Since the products obtained from amides are analogous to those produced from thiamides, it is probable that amides also exist in an unstable form, $\text{OH}\cdot\text{CX}\cdot\text{NH}$, in which they enter into the reaction. This conclusion is borne out by the fact that they only react at a higher temperature than do the thioamides.

Many derivatives of *selenazole* have also been prepared, and will be described later.

F. S. K.

Chloroformamide and its Use in Synthesis. By L. GATTERMANN (*Annalen*, **244**, 29—76).—The properties of chloroformamide and its preparation from carbonyl chloride and ammonium chloride have been previously described by the author and Schmidt (*Abstr.*, 1887, 569).

Analogous compounds are obtained by the action of carbonyl chloride on methylamine and ethylamine hydrochlorides. $\text{NHMe}\cdot\text{COCl}$ melts at 90° , and boils at 93 — 94° . $\text{NHEt}\cdot\text{COCl}$ boils at 92 — 93° , and dissociates into hydrogen chloride and ethyl isocyanate.

Chloroformamide is decomposed by an excess of absolute methyl alcohol, yielding methyl carbamate, but if the methyl alcohol is slowly added to an excess of the chloroformamide, methyl allophanate is produced. Similar reactions are exhibited by other alcohols. *Octyl allophanate* melts at 155 — 156° , and *cetyl allophanate* at 70° . An ethereal solution of ethylene chlorhydrin yields *chlorethyl carbamate*, $\text{NH}_2\cdot\text{COO}\cdot\text{C}_2\text{H}_4\text{Cl}$. It is deposited from hot water in colourless, highly refractive plates, and melts at 115° . *Ethylene carbamate* (from

glycol) is soluble in warm water, alcohol, and warm acetic acid. It melts at 147—149°. *Glyceryl carbamate*, $C_3H_5(O\cdot CONH_2)_3$, melts at 215°, *phenyl carbamate* at 143°, *α -naphthyl carbamate* at 158°, *β -naphthyl carbamate* at 187°, *orthophenylene carbamate* at 178°, the *meta*-compound at 194°, and the *para*-compound at 236°. Pyrogallol yields a carbamate, $C_6H_3(O\cdot CONH_2)_3$, melting at 178°. Salicaldehyde is converted by chloroformamide into "*disalicylaldehyde*," which is also the product of the action of acetic or benzoic chloride on the aldehyde. *Phenyl thioallophanate* melts at 218°.

The synthesis of several aromatic acids by the action of aluminium chloride and chloroformamide (or its homologues) on hydrocarbons diluted with carbon bisulphide, has already been described (*loc. cit.*). Similar results are obtained in the case of thio-compounds, thus: *β -thiotolene* yields an amide, melting at 119°, which is converted by saponification into methylthiophenic acid. *Metathioxene* yields an amide, $C_4SHMe_2\cdot CONH_2$, which crystallises in colourless needles, and melts at 115—116°. On hydrolysis, *dimethylthiophencarboxylic acid*, $C_4SHMe_2\cdot COOH$ [$Me_2 : COOH = 2 : 4 : 5$], is obtained; this crystallises in needles, and melts at 171—172°. From trimethylthiophene, an amide, $C_4SMe_3\cdot CONH_2$, melting at 146—147°, and *trimethylthiophencarboxylic acid*, [$Me_3 : COOH = 2 : 3 : 4 : 5$], are obtained. The acid forms thick prisms, and melts at 207—208°.

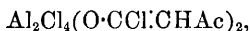
In accomplishing the synthesis of aromatic acids, ethers may be used instead of hydrocarbons; thus, anisic acid can be prepared from anisole, and paraethoxybenzoic acid from phenetole. *Orthocresyl methyl ether* yields an amide, $OMe\cdot C_7H_{10}\cdot CONH_2$, from which the acid $OMe\cdot C_6H_3Me\cdot COOH$ [$MeO : COOH = 1 : 2 : 4$] is derived. The acid melts at 193°, the amide at 144°. *Orthocresyl ethyl ether* yields analogous results. The amide melts at 167°, and the acid at 199°. *Paracresyl methyl ether* yields an amide, [$Me : CONH_2 : OMe = 1 : 3 : 4$], which crystallises in colourless needles, melts at 163°, and yields methoxyparahomosalicylic acid on hydrolysis.

The amide derived from thymyl methyl ether melts at 149°, and is saponified with difficulty, yielding the acid $OMe\cdot C_{10}H_{12}\cdot COOH$, which has been described by Leuckart and Schmidt. Chloroformamide acts on methylene phenyl ether in presence of aluminium chloride, yielding the amide $C_2H_4(O\cdot C_6H_4\cdot CONH_2)_2$. This substance melts at 280° with decomposition. The amide from *α -naphthyl methyl ether* melts at 232°, and that from *α -naphthyl ethyl ether* melts at 244°. The latter, on hydrolysis, yields *ethoxynaphthoic acid*, $OEt\cdot C_{10}H_8\cdot COOH$. This forms colourless needles, and melts at 214°. The amide from *β -naphthyl methyl ether* melts at 186°, and that from *β -naphthyl ethyl ether* crystallises in large plates, and melts at 161°. Neither of these *β -amides* could be saponified.

W. C. W.

Action of Aluminium Chloride on Acetic Chloride. By G. GUSTAVSON (*J. pr. Chem.* [2], **37**, 108—110).—The substance obtained by Combes (Abstr., 1887, 127, 656) by the interaction of aluminium chloride (1 mol.) with acetic chloride (6 mols.) has really the constitution $Al_2Cl_4(O\cdot CCl_2\cdot CHAc)_2$, and on treatment with alcohol gives ethyl acetylacetoacetate, $CHAc_2\cdot COOEt$ (James, Trans., 1885, 1).

In all probability, the compound $\text{Al}_2\text{Cl}_4(\text{O}\cdot\text{CCl}_2\cdot\text{CHAc})_2$ is formed by the direct addition of acetic chloride to the compound



which has been prepared by Winogradoff.

G. T. M.

Ethereal Amidoacetates. By T. CURTIUS and F. GOEBEL (*J. pr. Chem.* [2], **37**, 150—181).—The hydrochlorides of ethereal salts of amidoacetic acid (glycocine) are produced when perfectly dry hydrogen chloride is passed into pure alcohol (half a litre) in which finely divided glycocine hydrochloride (100 grams) is suspended. The *methyl amidoacetate hydrochloride*, $\text{NH}_2\cdot\text{CH}_2\cdot\text{COOMe}\cdot\text{HCl}$, forms large prisms melting at 175° . The platinochloride crystallises in orange-yellow plates, readily soluble in water and alcohol. *Ethyl amidoacetate hydrochloride*, $\text{NH}_2\cdot\text{CH}_2\cdot\text{COOEt}\cdot\text{HCl}$, crystallises in colourless needles melting at 144° , and on careful heating sublimes unchanged. The platinochloride forms needles, readily dissolved by water and alcohol, and melting at $211\text{--}212^\circ$. Allyl amidoacetate hydrochloride does not crystallise well. It forms glistening scales melting somewhere between 170° and 180° . The amyl amidoacetate hydrochloride, $\text{NH}_2\cdot\text{CH}_2\cdot\text{COOC}_5\text{H}_{11}\cdot\text{HCl}$, forms an oily syrup. The copper salts, $(\text{COOEt}\cdot\text{CH}_2\cdot\text{NH})_2\text{Cu} + 2\text{H}_2\text{O}$ and $(\text{COOMe}\cdot\text{CH}_2\cdot\text{NH})_2\text{Cu} + \text{H}_2\text{O}$, are formed when the hydrochlorides are boiled with freshly precipitated hydrated copper oxide. Ethyl amidoacetate, when distilled with soda, gives normal propylamine, the hydrochloride of which melts at $157\text{--}158^\circ$; hence its constitution must be $\text{NH}_2\cdot\text{CH}_2\cdot\text{COOEt}$, and not $\text{NH}\cdot\text{Et}\cdot\text{CH}_2\cdot\text{COOH}$.

The free ethereal salts are best obtained by shaking their hydrochlorides with ether and finely divided silver oxide. They can be purified by distillation under reduced pressure. *Ethyl amidoacetate*, $\text{NH}_2\cdot\text{CH}_2\cdot\text{COOEt}$, is a colourless, transparent liquid boiling at $148\text{--}149^\circ$ under a pressure of 748 mm., and at 65° under a pressure of 40 mm. It does not solidify at -20° . Vapour-density, 3.47; calculated, 3.57. It has strong basic properties, a characteristic odour resembling fresh cacao, and mixes with water, alcohol, ether, benzene, and chloroform. *Methyl amidoacetate*, $\text{NH}_2\cdot\text{CH}_2\cdot\text{COOMe}$, cannot be distilled at ordinary pressures without decomposition; under a pressure of 50 mm., it boils at 54° , and can be distilled without suffering change. In other respects, it greatly resembles the ethyl salt.

Glycocine anhydride, $\text{C}_2\text{H}_3\text{NO}$, is formed when ethyl amidoacetate is allowed to remain for some days with four times its own volume of water, or when the ether in aqueous solution is shaken with silver oxide. It crystallises in flat plates, and when quickly heated sublimes in beautiful, long needles, blackens at $245\text{--}260^\circ$, and seems to melt at 275° . Glycocine anhydride is neutral to litmus-paper, but forms compounds with acids, salts, and the heavy metals, and probably has the constitution $\text{CH}_2\cdot\text{N}(\text{CO})\text{H}$. The compounds it forms with silver, $\text{NaAgC}_2\text{H}_3\text{O}$, and copper are described. It forms a hydrochloride which crystallises from alcohol in long needles melting at $129\text{--}130^\circ$, and on boiling with water is converted into glycocine hydrochloride melting

at 180°. On distillation, ethyl amidoacetate leaves a residue, which, after boiling with charcoal and recrystallisation, has the formula $C_9H_{13}O_4N_5$. G. T. M.

Analogy between Alkyl-sulphonated Fatty Acids and Ketone Acids. By R. OTTO and W. OTTO (*Ber.*, **21**, 992—998; compare this vol., p. 360).—*Ethylsulphoneacetic acid*, $SO_2Et \cdot CH_2 \cdot COOH$.—The ethyl salt of this acid (Claesson, this Journal, 1877, ii, 297) is a thickish, slightly yellowish oil which is quickly hydrolysed by concentrated potash. The free acid forms a thick, colourless, odourless syrup, which, on heating at 180—190°, yields carbonic anhydride and methylethylsulphone (Beckmann, *Abstr.*, 1879, 37). The *sodium* salt is very readily soluble in water, and crystallises from boiling 90 per cent. alcohol in thin, nacreous leaves; it is only sparingly soluble in boiling absolute alcohol, and when heated to about 130°, it yields sodium carbonate and methylethylsulphone. When the acid is treated with bromine, carbonic anhydride and dibromomethylethylsulphone are produced; when treated with zinc and hydrochloric acid, it is reduced to ethyl mercaptan.

α-Ethylsulphonepropionic acid, $SO_2Et \cdot CHMe \cdot COOH$.—The ethyl salt is obtained by heating sodium ethylsulphinate with ethyl *α*-chloropropionate; it is a thick, yellowish oil of feeble ethereal odour, and is miscible with ether and alcohol in all proportions. The free acid is a thick, odourless, slightly yellow oil which is miscible with water and alcohol. It is decomposed into carbonic anhydride and diethylsulphone when heated to about 200°, or when heated with potash to about 150°. The *sodium* salt is readily soluble in water and alcohol.

β-Ethylsulphonepropionic acid, $SO_2Et \cdot CH_2 \cdot CH_2 \cdot COOH$, prepared by the action of sodium ethylsulphinate on *β*-iodopropionic acid, crystallises in small, shining leaves melting at 112°; it is very readily soluble in water, alcohol, and ether. The *sodium* salt is very readily soluble in water and alcohol. When the acid is heated to about 150° with a large excess of potash, it remains unchanged, but when the temperature is raised to 200° it is decomposed with formation of propionic acid and sulphur dioxide. When heated alone, the acid yields mercaptan, sulphur dioxide, and other products.

α-Phenylsulphonebutyric acid, $SO_2Ph \cdot CHEt \cdot COOH$, is obtained by the action of sodium benzenesulphinate on *α*-monobromobutyric acid; it crystallises in shining needles which melt at 123—124°, dissolves readily in ether and alcohol, but less readily in water. The *barium* salt is a gummy mass readily soluble in water, but insoluble in absolute alcohol. The *sodium* salt is amorphous.

When *α*-phenylsulphonebutyric acid is distilled, carbonic anhydride and propylphenylsulphone are produced; the latter compound crystallises from dilute alcohol in aggregates of nacreous leaves or scales which melt at 44°, dissolve readily in alcohol and benzene, but only sparingly in boiling water. Propylphenylsulphone is also formed when the acid is heated with an excess of potash at 100°. Bromine has no action on the aqueous solution of the acid.

From the above results, it follows that the fatty alkyl-sulphonic acids which contain alcohol radicles of the methane series, and are

comparable with the β - and γ -ketone acids, obey the same laws as similar acids which contain aromatic alcohol radicles (this vol., p. 360); this is probably also true for similarly constituted fatty acids belonging to the α -series, $\text{SO}_2\text{R}\cdot\text{COOH}$. F. S. K.

Occurrence of Lignoceric and Arachidic Acids in Earth-nut Oil. By P. KREILING (*Ber.*, **21**, 880—881).—The author finds that lignoceric acid, first prepared by Hell and Hermann from beech-tar (Abstr., 1881, 249), occurs in earth-nut oil. He also confirms Gössmann's statement (*Annalen*, **89**, 1) that arachidic acid occurs in this oil.

Occurrence of Oleic Acid in Earth-nut Oil. By L. SCHON (*Ber.*, **21**, 878—879).—The author has examined specimens of earth-nut oil, both commercial and prepared by himself from the nuts, and finds that the only acid of the oleic series contained therein is ordinary oleic acid. This is contrary to the statements of Gössman and Scheven (*Annalen*, **94**, 230) and of Schröder (*ibid.*, **143**, 22) that hypogæic acid occurs in this oil.

The following formulæ are quoted for new oleates, no description of which are, however, given: $\text{LiC}_{18}\text{H}_{33}\text{O}_2$; $\text{Pb}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2 \cdot 2\text{PbO}$; $\text{Mn}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2$; $\text{Fe}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2$; $\text{Al}_2(\text{C}_{18}\text{H}_{33}\text{O}_2)_6$. A. J. G.

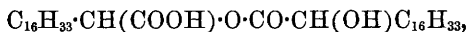
Action of Strong Sulphuric Acid on Oleic Acid and Triolein. By A. C. GEITEL (*J. pr. Chem.* [2], **37**, 53—90).—The author has investigated the behaviour of strong sulphuric acid with both oleic acid and tri-olein. The reaction is an exceedingly indefinite one, neither the oleic acid nor the tri-olein becoming completely saturated even in presence of a large excess of sulphuric acid. The chief product in the case of oleic acid is an acid ethereal salt, in that of tri-olein a normal ethereal salt. The extent to which combination had taken place was ascertained by titrating the products with solutions of potash and iodine of known strength.

When one molecule of sulphuric acid is mixed with one molecule of oleic acid at low temperatures, about one-third of the oleic acid is converted into α -stearinsulphuric acid, $\text{C}_{15}\text{H}_{31}\cdot\text{CH}_2\cdot\text{CH}(\text{SO}_3\text{H})\cdot\text{COOH}$, which forms a brown viscid fluid readily dissolved by water, alcohol, and ether, but insoluble in dilute acids, and in solutions of Glauber's salt. The potassium salt, $\text{C}_{15}\text{H}_{31}\cdot\text{CH}_2\cdot\text{CH}(\text{SO}_3\text{K})\cdot\text{COOK}$, is a bright-brown, greasy soap, soluble in water, alcohol, and ether. The sodium salt is likewise an oil. The barium salt, $\text{C}_{15}\text{H}_{31}\text{SO}_6\text{Ba}$, forms an amorphous, white powder, insoluble in water, but readily dissolved by alcohol and ether. On boiling with acetic acid, it gives the acid salt, $(\text{COOH}\cdot\text{C}_{17}\text{H}_{33}\cdot\text{SO}_4)_2\text{Ba}$. Three copper salts are described.

Another product of the action of sulphuric acid on oleic acid is an anhydride of the formula $\text{C}_{14}\text{H}_{29}\cdot\text{CH} < \begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{O} \text{---} \text{CO} \end{smallmatrix} >$. This crystallises in small, white scales, melting at 47—48°. The calcium and lead salts of the acid are described.

When α -stearinsulphuric acid is boiled with dilute acids, α -hydroxy-stearic acid, $\text{C}_{15}\text{H}_{31}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{COOH}$, is formed; this is a crystalline solid, melting at 81—81.5°, and dissolves readily in alcohol

and ether. The calcium, lead, and copper salts are described. The acid readily loses water, forming first the monobasic acid,



and by further loss the anhydride, $\text{C}_{16}\text{H}_{33}\cdot\text{CH}<\begin{smallmatrix}\text{CO}\cdot\text{O}\\\text{O}\cdot\text{CO}\end{smallmatrix}>\text{CH}\cdot\text{C}_{16}\text{H}_{33}$.

It is an exceedingly difficult matter to isolate the products of the action of sulphuric acid on the tri-olein. When those substances are carefully brought together in the ratio of 3 mols. of the former to 1 mol. of the latter, the chief final product is a monobasic acid of the formula $\text{C}_{16}\text{H}_{33}\cdot\text{CH}(\text{SO}_4\text{H})\text{COO}\cdot\text{C}_3\text{H}_5(\text{O}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_{16}\text{H}_{31})\cdot\text{O}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{C}_{16}\text{H}_{33}$. The barium and copper salts form oils which are readily decomposed by potash. G. T. M.

Constitution of Acetoacetic, Succinosuccinic, and Quinone-hydrodicarboxylic Acids. By A. GEUTHER (*Annalen*, 244, 190—221).—The author maintains that the acetoacetic and succinosuccinic acids are not ketonic acids, and he points out that the results obtained by Israel (Abstr., 1886, 334, and 1887, 915) and by Isbert (Abstr., 1886, 1009) are evidence in favour of the formula $\text{CH}_3\text{C}(\text{OH})\cdot\text{CH}\cdot\text{COOEt}$ for ethyl acetoacetate.

The author criticises Ebert's experiments (Abstr., 1885, 1122) on the constitution of succinosuccinic acid, and complains that Baeyer has incorrectly represented his views on this subject (Abstr., 1886, 223 and 445). W. C. W.

Methyl Acetocyanacetate. By A. HALLER and A. HELD (*Compt. rend.*, 106, 210—213).—*Methyl acetocyanacetate*, $\text{CN}\cdot\text{CHAc}\cdot\text{COOMe}$, was obtained in the same way as the ethyl-derivative (Abstr., 1887, 799 and 1029), by the action of cyanogen chloride on a mixture, in molecular proportions, of methyl acetoacetate and sodium methoxide, dissolved in excess of methyl alcohol. It crystallises from ether in silky needles which melt at $46\cdot5^\circ$ and dissolve readily in ether or alcohol, but are insoluble in water.

The sodium-derivative, $\text{C}_6\text{H}_5\text{NaNO}_2$, is obtained by the action of sodium carbonate in alcoholic solution. It forms white, silky, anhydrous crystals soluble in water and alcohol. The calcium-derivative, prepared in a similar way, forms bulky, transparent, efflorescent crystals containing 6 mols. H_2O .

Methyl acetocyanacetate can also be prepared by mixing a solution of methyl sodiocyanacetate in methyl alcohol, with a solution of acetyl chloride in ether, and heating at $40\text{--}50^\circ$ for some hours; the product is then treated with acidified water, submitted to fractionation in a vacuum, and the ethereal salt converted into its calcium-derivative.

If sodium ethoxide is used in place of the methoxide in the first method, the product is an uncrystallisable mixture of ethyl and methyl acetocyanacetates which cannot be separated by fractionation. It is evident that double decomposition takes place between the ethoxide and the methyl acetocyanacetate with formation of a mixture of methyl and ethyl salts. Purdie has observed a similar reaction in the case of the ethereal salts of fumaric, oxalic, and other acids (Trans.,

1887, 627), and Peters in the case of methyl and ethyl acetoacetates (this vol., p. 254). C. H. B.

Compounds of Ethylidenelactic Acid. By R. LEIPEN (*Monatsh.*

Chem., **9**, 45—51).—*Ethylidene lactate*, $\begin{matrix} \text{CHMe}\cdot\text{O} \\ \text{CO}\text{---}\text{O} \end{matrix} \text{CHMe}$, is obtained by heating acetaldehyde with an excess of lactic acid (previously partially converted by heating at above 150° into anhydride and lactide), for some hours at 120° to 170° . The product is distilled, and the portion boiling between 50° and 200° is treated with potassium carbonate, when the ether separates. It is a clear liquid of a slightly ethereal odour, boils at $150\text{--}151.5^\circ$, and dissolves in a large amount of water. Hot water decomposes it quickly into its constituents.

Lactanilide, $\text{C}_9\text{H}_{11}\text{NO}_2$, is prepared by heating lactic acid and aniline for six to seven hours on a sand-bath at such a temperature that water is given off, the liquid not being allowed to boil. The product is extracted with boiling water, and the filtered extract concentrated by evaporation. It crystallises in colourless plates, melting at 58° , readily soluble in alcohol, ether, and chloroform, but insoluble in light petroleum. Boiling dilute aqueous soda decomposes it.

Lactoparatoluide, $\text{C}_{10}\text{H}_{13}\text{NO}_2$, prepared in a manner similar to the anilide, crystallises in needles, melting at $102\text{--}103^\circ$, very sparingly soluble in cold water. The *orthotoluide* is purified by allowing the solution in benzene to evaporate slowly, when it separates as a white powder, melting at 72° . Both toluides resemble the anilide in solubility.

N. H. M.

Galactosecarboxylic Acid. By MAQUENNE (*Compt. rend.*, **106**, 286—288).—If a solution of galactose is mixed with hydrocyanic acid at the ordinary temperature, its rotatory power gradually disappears, and the liquid becomes brown. A concentrated solution deposits a yellowish, slightly soluble, crystalline precipitate, especially if the excess of hydrocyanic acid is expelled by a current of air. This precipitate is the amide of galactosecarboxylic acid, $\text{C}_7\text{H}_{15}\text{NO}_7$, and may be purified by crystallisation from boiling acetic acid, from which it separates in slender, yellowish, microscopic needles, slightly soluble in water, and almost insoluble in alcohol, but soluble in boiling acetic acid. It melts at 194° with partial decomposition.

When boiled with water, and especially with alkalis, the amide is readily decomposed with liberation of ammonia and formation of a salt of the acid. The formation of an amide shows that the action of hydrocyanic acid on galactose is not strictly analogous to its action on levulose.

Galactosecarboxylic acid, $\text{C}_7\text{H}_{14}\text{O}_8$, is most readily prepared by decomposing its barium salt with sulphuric acid, and evaporating in a vacuum. It forms slender needles which melt at 145° and decompose at a higher temperature. It has a distinctly acid taste and reaction, and is soluble in water, but almost insoluble in absolute alcohol. Barium galactosecarboxylate, obtained by the action of barium hydroxide on the amide, forms long, slender, microscopic needles, which dissolve slowly in water, and are insoluble in alcohol. It is slightly dextrogyrate $[\alpha]_D = 5^\circ 30'$.

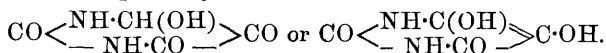
This action of hydrocyanic acid shows that galactose has an aldehydic or ketonic function. C. H. B.

Action of Hydrocyanic Acid on Galactose. By H. KILIANI (*Ber.*, **21**, 915—919; compare preceding Abstract).—When finely powdered galactose (30 grams), moistened with water (6 c.c.), is treated with the calculated quantity of 50 per cent. hydrocyanic acid and a few drops of ammonia, and allowed to remain at the ordinary temperature in a perfectly closed flask, solution of the carbohydrate occurs and at the end of eight hours a rise in the temperature of the liquid takes place accompanied by the separation of the *amide* of galactosecarboxylic acid in small, white needles. The yield amounts to 40—50 per cent. of the weight of the galactose employed.

Galactosecarboxylic acid, $C_6H_{13}O_6 \cdot COOH$, is prepared from the amide by digesting it with milk of lime at 100° to expel ammonia, decomposing the resulting basic calcium salt with oxalic acid, and evaporating the filtrate over sulphuric acid in a vacuum. It crystallises in slender needles, and melts at 145° with the loss of 2 mols. H_2O and the formation of an amorphous *anhydride*; a similar decomposition also occurs when the aqueous solution of the acid is boiled for some time. The *potassium* salt, $2C_6H_{13}O_6 \cdot COOK + H_2O$, crystallises in colourless prisms or needles, and fuses at 110° with the loss of its water of crystallisation; the *calcium* salt was also prepared. On reduction with concentrated hydriodic acid and amorphous phosphorus for $1\frac{1}{2}$ hours in a reflux apparatus, the acid is converted into the lactone of normal γ -hydroxyheptylic acid (b. p. = 231°), and a very small quantity of normal heptylic acid, consequently galactosecarboxylic acid, like dextrosecarboxylic acid, must be regarded as a normal hexahydroxyheptylic acid. W. P. W.

Synthetical Experiments in the Uric Acid Series. By R. BEHREND and O. ROOSEN (*Ber.*, **21**, 999—1001).—Further experiments have shown that one of the products obtained by the reduction of nitrouracil (Behrend, *Annalen*, **229**, 39), is the ureid of an α - β -dihydroxyacrylic acid or *isobarbituric acid*, $CO < \begin{smallmatrix} NH \cdot CH \\ NH \cdot CO \end{smallmatrix} > C \cdot OH$.

Hydroxylamine does not act on this compound, but when it is boiled with acetic anhydride, an acetyl-derivative is formed which crystallises from hot water in the form of sparingly soluble, colourless, concentrically grouped prisms. When isobarbituric acid is treated with bromine-water, it yields an acid which has the same composition as dialuric acid. This substance crystallises in solid prisms with 2 mols. H_2O , the first of which passes off at 100° , the second at 140 — 150° , apparently with slight decomposition. It differs from ordinary dialuric acid in crystalline form, water of crystallisation, and in its ready solubility in water as well as in its stability towards oxidising agents, it may therefore be termed *isodialuric acid*, and its formula is probably either



This acid is also formed by the action of bromine-water on amido-

uracil and hydroxyxanthine. It is readily acted on by acetic anhydride. When heated with carbamide and concentrated sulphuric acid, a white, crystalline powder is obtained, the analysis of which agreed with that of uric acid. The compound is an acid, decomposes carbonates and gives the murexide reaction; it reduces Fehling's solution, and a dilute solution in sodium carbonate blackens paper moistened with silver nitrate. It crystallises from hot water in the right-angled plates which are characteristic of uric acid. The solubility in water at 18° was found to be 1:9000. The sodium salt, $C_5H_3N_4O_3Na \cdot \frac{1}{2}H_2O$, crystallises in microscopic needles. The barium salt, $(C_5H_3N_4O_3)_2Ba \cdot 2H_2O$, is amorphous. F. S. K.

Trimethyluracil. By M. HAGEN (*Annalen*, **244**, 1—19).—The preparation of trimethyluracil by the action of methyl iodide on the potassium salt of methyluracil at 150°, has been described by Behrend (*Abstr.*, 1886, 339). The excess of methyl iodide is removed from the crude product by distillation, and the residue is dissolved in water. The solution is agitated with chloroform, and sodium carbonate is added to the chloroform extract to remove free iodine. The residue which is left after distilling off the chloroform is treated with ether; the trimethyluracil slowly dissolves leaving a small residue of methyluracil dihydride.

Trimethyluracil crystallises in rhombic plates and melts at 109°. It does not form salts with acids or with bases. It is decomposed by barium hydroxide at 200°, yielding methylamine, and carbonic and acetic acids. Its constitution is probably represented by the formula $CO < \begin{smallmatrix} NMe \cdot CMe \\ NMe \cdot CO \end{smallmatrix} > CH$. Benzyl chloride acts on the potassium salt of methyl uracil, forming *benzylmethyluracil*, a crystalline compound melting at 232—233°.

Dry bromine or a solution of bromine in carbon bisulphide acts on dry trimethyluracil, forming a compound of the composition $C_6H_9NO_4Br_2$. *Dibromhydroxytrimethyluracil* is obtained as a white powder when bromine is added to an aqueous solution of trimethyluracil. It is deposited from a hot aqueous solution in rhombic plates, and melts at 163° with decomposition. It is decomposed by prolonged boiling with alcohol, yielding bromotrimethyluracil. This substance melts at 126°.

Dichlorhydroxytrimethyluracil melts with decomposition at 143—144°. It is converted into *chlorotrimethyluracil* by the action of stannous chloride.

Amidotrimethyluracil is formed by acting on bromotrimethyluracil with strong ammonia at 140°. It melts at 166—167°, is soluble in water, and forms deliquescent salts. The hydrochloride interacts with an excess of potassium cyanate, forming *trimethylhydroxyxanthine* in small quantities; this crystallises in microscopic prisms.

W. C. W.

Cyanuric Derivatives of Taurine. By B. RATHKE (*Ber.*, **21**, 874—877).—When a solution of the hydrochloride of ethylenethiameline (*Abstr.*, 1887, 650) is treated with chlorine, a nearly insoluble compound separates in silvery plates; this seems to be an *inner*

anhydride of taurammeline of the formula

$$\begin{array}{c} \text{N} \cdot \text{C}(\text{OH}) \cdot \text{N} \cdot \text{C}_2\text{H}_4 \\ | \qquad \qquad | \\ \text{C}(\text{NH}_2) \cdot \text{N} \cdot \text{C} = \text{N} \end{array} \text{SO}_2;$$

it dissolves in alkalis, presumably with conversion into the sulphonic acid, but is reprecipitated on addition of acids; with silver nitrate, it gives a white precipitate sparingly soluble in ammonia.

Taurodiammeline, $\text{C}_{10}\text{H}_{15}\text{N}_9\text{S}_2\text{O}_8$, is formed at the same time as the above compound, but is formed alone when the ethylenethiammeline is oxidised with nitric acid. It forms slender, transparent prisms, sparingly soluble in cold water; when heated, it begins to turn brown at 270° , but is still not melted at 290° . It has very marked acid characters; the salts with the alkalis and alkaline earths are readily soluble.

Taurammelide, $\text{NH}_2 \cdot \text{C} \begin{array}{c} \text{N} \cdot \text{C}(\text{OH}) \\ \text{N} \end{array} \text{CO} > \text{N} \cdot \text{C}_2\text{H}_4 \cdot \text{SO}_3\text{H}$, is obtained on boiling the preceding compound with baryta-water; it forms sparingly soluble crystals, and melts at $265\text{--}270^\circ$ with decomposition.

A. J. G.

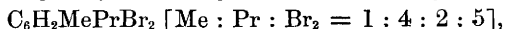
Vapour-density of Aluminium Methide. By E. LOUISE and L. ROUX (*Compt. rend.*, **106**, 602—603).—The aluminium methide was prepared by the action of mercuric methide on excess of aluminium, and was redistilled over aluminium in pure and dry nitrogen. It is a colourless mobile liquid which boils at 140° , and is much less stable than aluminium ethide. The vapour-density was determined by Meyer's method at different temperatures.

Temperature	182°	216°	310°	340°	440°
Vapour-density	5.1	4.75	4.6	2.4	1.8

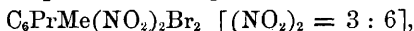
At 50° above the boiling point, the vapour-density agrees with the formula Al_2Me_6 , but as the temperature rises, the compound gradually decomposes until at 440° the vapour-density is only 1.8. The products of decomposition are metallic aluminium and gaseous paraffins and olefines.

C. H. B.

2 : 5 Dibromocymene. By A. CLAUS (*J. pr. Chem.* [2], **37**, 14—27; see Abstr., 1880, 632; *Ber.*, **13**, 905, 972).—By direct bromination of paracymene, only one dibromoparacymene,



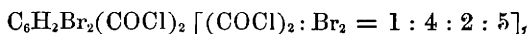
is obtained, which when nitrated with a mixture of nitric and sulphuric acids furnishes three nitro-derivatives, melting at 149° , 142° , and 89° respectively. The product melting at 149° has the formula—



crystallises from alcohol in colourless needles, and is characterised by great stability. It is only imperfectly decomposed by heating with fuming nitric acid in sealed tubes at 280° , and is scarcely attacked by long-continued boiling with aqueous or alcoholic potash. The compound melting at 142° crystallises from ordinary solvents in yellow needles or prisms, and sublimes in small scales. It is a *dibromodinitrotoluene*, $\text{C}_6\text{HMe}(\text{NO}_2)_2\text{Br}_2$ [Me : Br₂ : (NO₂)₂ = 1 : 2 : 5 : 4 : 6], and is readily attacked by potash. With aniline, it readily forms the compound $\text{NHPh} \cdot \text{C}_6\text{HMeBr}(\text{NO}_2)_2$, crystallising in glistening

orange-red needles, melting at 116° . The third product melting at 89° is only formed in small quantity, but is practically the sole product of nitrating dibromocymene with fuming nitric acid at 100° . It is a dibromonitrotoluene, $C_6H_2Br_2Me \cdot NO_2$ [$Me : Br_2 : NO_2 = 1 : 2 : 5 : 4$], and can be readily further nitrated with formation of the compound above described melting at 142° . It is very soluble in petroleum and alcohol, from which it crystallises in long, colourless needles, and is identical with the substance described by Nevile and Winther (*Trans.*, 1880, 429); and furnishes by reduction first a dibromotoluidine (m. p. $83-85^{\circ}$) and finally toluidine. The formation of dibromodinitrotoluene (m. p. 142°) by nitration of paracycymene is remarkable, the propyl-group being oxidised and then replaced by a nitro-group.

When dibromocymene is heated in sealed tubes for eight hours at 180° with 20 times its weight of nitric acid of sp. gr. 1.12, it is converted into dibromoterephthalic acid, which on treatment with phosphorus pentachloride yields a chloride—



readily soluble in carbon bisulphide and chloroform, and crystallising from ether in prisms melting at $80-81^{\circ}$. The corresponding amide, $C_6H_2Br_2(CONH_2)_2$, is insoluble in alcohol, ether, chloroform, and light petroleum, but dissolves sparingly in carbon bisulphide, from which it crystallises in fine needles; these carbonise at 300° without previously melting. By gentle oxidation, dibromocymene yields a monobasic acid of the formula $C_{10}H_{10}Br_2O_2$. The sodium salt forms beautiful colourless needles. The ammonium salt is only slightly soluble in water, and melts at 172° . The calcium salt crystallises in stellate groups of needles with 4 mols. of water, whilst the silver salt separates from a hot aqueous solution in needles containing 3 mols. H_2O . This acid is either dibromocumic acid, $C_6H_2PrBr_2 \cdot COOH$ [$COOH : Pr : Br_2 = 1 : 4 : 3 : 6$], or dibromotolylpropionic acid, $C_6H_2Br_2Me \cdot C_2H_4 \cdot COOH$. The author gives reasons in favour of its being the latter.

G. T. M.

Derivatives of 1 : 2 : 3 : 4 Tetramethylbenzene (Prehnitene).

By A. TÖHL (*Ber.*, 21, 904—908).—Prehnitene combines with picric acid to form a fairly stable compound, which crystallises from alcohol in yellow needles and melts at $92-95^{\circ}$.

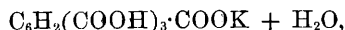
Nitroprehnitene, $C_{10}H_{13} \cdot NO_2$, is obtained when a thin layer of prehnitene is allowed to remain in contact with ordinary nitric acid for three to four days, and is purified by distillation with steam. It crystallises in stellate groups of flat needles, melts at 61° , boils with partial decomposition at 295° (thermometer in vapour), and is readily soluble in ether, alcohol, light petroleum, and acetic acid. On reduction with iron and acetic acid, it yields *prehnidine*, $C_{10}H_{13} \cdot NH_2$. This crystallises in large, lustrous, colourless scales, melts at 70° , is readily soluble in alcohol, ether, and light petroleum, and is volatile with steam. The *hydrochloride*, $C_{10}H_{13} \cdot NH_2 \cdot HCl$, crystallises from water in tufts of very long, colourless needles; the *sulphate*, $(C_{10}H_{13} \cdot NH_2)_2 \cdot H_2SO_4$, crystallises in large scales, and is sparingly soluble in cold water; the *nitrate* crystallises from water in six-cornered prisms. *Acetoprehnidine*, $C_{10}H_{13} \cdot NHAc$, crystallises from

dilute alcohol in colourless needles, melts at 172° , is readily soluble in alcohol, and on treatment with ordinary nitric acid yields the *nitro*-derivative, $\text{NO}_2 \cdot \text{C}_{10}\text{H}_{12} \cdot \text{NHAc}$. This compound can also be obtained by the action of acetic chloride on nitroprehnidine, and crystallises from dilute alcohol in hair-like, branching needles, melting at 225° . When reduced with tin and hydrochloric acid, it is converted into *ethenylprehnityleneamidine hydrochloride*, $\text{C}_{10}\text{H}_{12} \left\langle \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} \right\rangle \text{CMe}, \text{HCl} + 2\text{H}_2\text{O}$, which crystallises in slender, colourless needles, and is readily soluble in water; the base is flocculent and contains 2 mols. H_2O .

Nitroprehnidine, $\text{NO}_2 \cdot \text{C}_{10}\text{H}_{12} \cdot \text{NH}_2$, is prepared by the reduction of dinitroprehnitene (Abstr., 1886, 694) with alcoholic ammonium sulphide. It crystallises in lustrous, red needles, melts at 131° , and is soluble in alcohol and concentrated hydrochloric acid. On reduction, it yields *prehnitylenediamine*, $\text{C}_{10}\text{H}_{12}(\text{NH}_2)_2$, which crystallises from water in large, lustrous scales, from alcohol in long, colourless needles, melts at 140° , is sparingly soluble in ether and light petroleum, and gives the reactions characteristic of an orthodiamine. The *hydrochloride*, $\text{C}_{10}\text{H}_{12}(\text{NH}_2)_2 \cdot 2\text{HCl} + \text{H}_2\text{O}$, crystallises in large, lustrous scales, and in dilute aqueous solution is coloured dark-red by ferric chloride and by potassium chromate.

Prehnitol, $\text{C}_{10}\text{H}_{13} \cdot \text{OH}$, obtained by fusing sodium prehnitenesulphonate with potassium hydroxide, crystallises from light petroleum in very long, colourless, silky needles, melts at 86 – 87° , boils at 266° (thermometer in vapour), and is very readily soluble in alcohol and ether. It is not coloured by ferric chloride. The *acetyl*-derivative, $\text{C}_{10}\text{H}_{12} \cdot \text{OAc}$, crystallises in large, well-formed prisms, and melts at 56 – 57° ; the *bromo*-derivative, $\text{C}_{10}\text{H}_{12} \cdot \text{Br} \cdot \text{OH}$, crystallises in long, slender needles, and melts at 151° .

When oxidised with a dilute aqueous solution of permanganate at 100° , prehnitene is first converted into prehnitylic acid (*loc. cit.*), and finally yields prehnitic acid; a *potassium* salt of the latter,



was obtained by treating the oxidation-product, after filtration, with acetic acid and lead acetate, decomposing the lead salt with hydrogen sulphide, and evaporating the filtrate; it crystallises in large aggregates. W. P. W.

Bromodichlorophenol and Dibromodichlorobenzene. By L. GARZINO (*Chem. Centr.*, 1887, 1546–1547; from *Rend. Acc. Lincei* [4], 3, 202–209).—*Bromometadichlorophenol*, $\text{C}_6\text{H}_2\text{BrCl}_2 \cdot \text{OH}$ [$? \text{OH} : \text{Cl}_2 : \text{Br} = 1 : 2 : 4 : 6$], is obtained by adding the calculated quantity of bromine to a cooled solution of dichlorophenol (15 grams) in glacial acetic acid (10 grams). The separation of the product causes the mass to become semisolid. It is exposed to the air until the small excess of bromine has volatilised, then washed with plenty of water, dried, distilled in a vacuum, and finally sublimed. The pure product forms white needles, melting at 68° , and boiling with decomposition at 268° . Under a pressure of 200 mm., it distils unchanged at 220° . It sublimes moderately well at 130 – 140° . It is readily soluble in benzene,

ether, and chloroform, also in concentrated acetic acid and alcohol, but is nearly insoluble in water. It is carried over with water vapour. Ferric chloride produces a light-blue colour in an alcoholic solution, but no colour in watery solution. It has hardly any smell and very little caustic action. No isomeride seems to be formed. Ammonium, sodium, potassium, barium, and silver salts, as well as the benzoate (m. p. 67·5°) and phthalate (m. p. 216—217°), were prepared.

For the preparation of *dibromodichlorobenzene*, $C_6H_4Br_2Cl_2$ [$? = 1 : 6 : 2 : 4$], a mixture of 20 grams of the above bromodichlorophenol, and 45 grams of phosphorus pentabromide was slowly distilled. The part distilling between 200° and 350° was heated with a 25 per cent. solution of potash, dried, and repeatedly crystallised from a mixture of light petroleum (b. p. 30—80°).

The pure product forms needles melting at 67—68°, very easily soluble in ether, light petroleum, and benzene. These crystals can be moderately easily sublimed. Besides this, another product is formed in small quantity, melting at 190·5—192°; this dissolves easily in ether and light petroleum, separates from benzene in small needles, and contains both chlorine and bromine. J. P. L.

Compounds of Phenoxides with Cuprous and Mercurous Chlorides. By A. G. POUCHET (*Compt. rend.*, **106**, 276—277).—A solution of phenol in sodium hydroxide when mixed with mercuric chloride yields a white precipitate of the composition $(C_6H_5O)_2Hg, Hg_2Cl_2 + 4H_2O$. β -Naphthol and α -anthrol yield respectively the compounds $(C_{10}H_7O)_2Hg, Hg_2Cl_2 + 4H_2O$ and $(C_{14}H_9O)_2Hg, Hg_2Cl_2 + 4H_2O$.

Strictly analogous compounds of cuprous chloride are obtained in precisely the same way. C. H. B.

Action of Aniline on Epichlorhydrin. By A. FAUCONNIER (*Compt. rend.*, **106**, 605—607).—Aniline (3 mols.) was heated at 140° and gradually mixed with epichlorhydrin (1 mol.). If the two liquids are first mixed and then heated, the reaction becomes explosively violent below 100°. The product is a brownish oil, which is dissolved in hydrochloric acid and reprecipitated by ammonia to remove aniline. The base is dissolved in ether, washed with water, then extracted with dilute hydrochloric acid, and the solution concentrated to a syrup, which gradually crystallises. It is purified by recrystallisation from alcohol. The hydrochloride thus obtained, $C_{15}H_{20}N_2Cl_2O$, forms colourless needles, very soluble in water, and somewhat soluble in alcohol, especially on boiling, but insoluble in ether. They become brown at 180°, soften at 196°, and melt with decomposition at 201—202°. The base is obtained by treating the hydrochloride with alkaline hydroxides, carbonates, or hydrogen carbonates, or even with sodium acetate, and forms a colourless, non-crystallisable oil, soluble in alcohol or ether, but insoluble in water. It seems to be isomeric with the dianilinehydrin obtained by Claus by the action of aniline on glycerol dichlorhydrin. The author proposes to call it *dianilglycerol*, and ascribes to it the constitution $NHPh \cdot CH_2 \cdot CH(NHPh) \cdot CH_2 \cdot OH$. It gives the general reactions for alkaloids, and reduces auric chloride and potassium ferricyanide in the cold. It gives a precipitate with

mercuric chloride only in presence of sodium carbonate. The platinum-chloride forms pale-yellow lamellæ. Picric acid produces an amorphous, yellow precipitate soluble in acids; bromine-water or sodium hypochlorite, a dull green precipitate; potassium dichromate an intense brown coloration; potassium permanganate a very intense violet coloration. C. H. B.

Metahydroxy-paranitrosodiphenylamine. By L. KOHLER (*Ber.*, 21, 908—910).—*Metahydroxydiphenylnitrosamine*, $C_{12}H_{10}N_2O_2$, is obtained by dissolving hydroxydiphenylamine in alcohol, and adding the calculated quantities of dilute sulphuric acid and of an aqueous solution of sodium nitrite to the well-cooled solution. It crystallises in slender, yellow needles, melts with decomposition at 115° , and is readily soluble in ether, alcohol, and acetic acid, soluble in benzene and light petroleum. When it is dissolved in a mixture of 2 parts by weight of absolute alcohol and 7 parts of ether, and heated in the cold with 1 part of alcoholic hydrogen chloride, brown scales of a hydrochloride separate, from which *metahydroxy-paranitrosodiphenylamine*,

$OH \cdot C_6H_5 \begin{array}{c} \text{NHPH} \\ | \\ \text{N} \end{array} \text{O} [NHPH : OH : N = 1 : 3 : 4]$, can be obtained by

suspending them in water, adding a slight excess of aqueous soda, and precipitating the filtrate with carbonic anhydride. It crystallises from benzene in beautiful, red needles, and is soluble in acetone, benzene, and alcohol, sparingly soluble in ether, and very sparingly soluble in light petroleum. Ammonia and aqueous soda dissolve it readily, and its solution in concentrated sulphuric acid is coloured red. On reduction with tin and hydrochloric acid at the ordinary temperature, it yields *metahydroxyparamidodiphenylamine*, $C_{12}H_{12}N_2O$, which crystallises in pale bluish scales, melts at 135° , and is readily soluble in alcohol, chloroform, and acetone, soluble in benzene and ether, and very sparingly soluble in light petroleum.

Hydroxyazophenine, $C_{26}H_{24}N_4O$, is formed by heating metahydroxy-paranitrosodiphenylamine with aniline and aniline hydrochloride at 100° for three hours. It crystallises from toluene in brown needles, melts at 197° , is insoluble in aqueous, but soluble in alcoholic potash and soda, and dissolves in concentrated sulphuric acid with a reddish-brown colour. W. P. W.

Condensation of Chloral Hydrate with Secondary Aromatic Amines. By P. BOESSNECK (*Ber.*, 21, 782—783).—With aniline, chloral hydrate yields trichlorethylidenediphenylamine, with elimination of water (Wallach, this Journal, 1872, 611; Cech, *ibid.*, 1876, ii, 66), whilst tertiary amines undergo the aldol-condensation with chloral hydrate (Boessneck, *Abstr.*, 1883, 976; 1884, 458. Knofer and Boessneck, this vol., p. 267); the reaction with secondary amines is now shown to be similar to that of the tertiary compounds.

Methylamidophenylhydroxytrichlorethane, $CCl_3 \cdot CH(OH) \cdot C_6H_4 \cdot NHMe$, is obtained by mixing chloral hydrate and methylaniline in molecular proportion, moderating the violent reaction by cooling, and afterwards allowing the mixture to remain at about 40 — 50° for

24 hours; it is then supersaturated with ammonia, distilled with steam to remove unaltered methylaniline, and the hydrochloride precipitated by addition of concentrated hydrochloric acid; after washing with alcohol and recrystallising from hot water, this is decomposed by ammonia. It is crystalline, and melts with decomposition at 112° . The hydrochloride forms thick prisms, sparingly soluble in cold water. The nitroso-compound, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{NO}$, prepared by the action of sodium nitrite on the hydrochloride, crystallises in needles, melts at $117\text{--}118^{\circ}$, begins to decompose at 140° , and is soluble in alcohol, acetic acid, and ether.

Ethylamidophenylhydroxytrichlorethane, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{NHEt}$, prepared in a manner similar to the methyl compound, is crystalline, and melts at 98° . The hydrochloride forms stellate group of needles, the nitroso-compound melts at 138° . A. J. G.

Reaction between Metaphenylenediamine and Carbon Bisulphide. By P. GUCCI (*Chem. Centr.*, 1887, 1547; from *Atti Soc. Toscano Sc. Nat.*, 5, 291—293).—*Thiocarbonylmetaphenylenediamine* thiocarbonate separates out in crystals after heating metaphenylenediamine and carbon bisulphide in sealed tubes for six hours with alcohol at $50\text{--}55^{\circ}$. After six hours' heating at 100° , a small quantity of a golden-yellow compound is formed in addition to the above. A further six hours' heating at 150° results in the latter substance alone being formed. The crystals are monoclinic, and do not give off hydrogen sulphide when boiled with alcohol. This compound is insoluble in water, ether, benzene, carbon bisulphide, and chloroform, and only sparingly soluble in ethyl and amyl alcohols.

At 280° , it remains unchanged, turns brown at 300° , and decomposes at a higher temperature. The author regards the compound as *sulphocarbonylmetaphenylenediamine*, $\text{C}_6\text{H}_4\cdot\text{N}_2\text{H}_2\cdot\text{CS}$. J. P. L.

Diazo-compounds. By P. GRIESS (*Ber.*, 21, 978—984).—The author has experimented on the behaviour of the three isomeric diazobenzoic acids towards methyl and ethyl alcohols and phenol. In the first two cases, 1 part of the acid, in the form of sulphate, was heated with 10 parts of the alcohol until the evolution of nitrogen ceased; in the experiments with phenol, 1 part of the sulphate was added to 2 to 3 parts of phenol, heated to its melting point, and the well-mixed mass warmed gently until the commencement of the reaction, which is always very energetic.

By methyl alcohol, metadiazobenzoic acid is completely converted into methylmetahydroxybenzoic acid. The product crystallises in white needles, which are very sparingly soluble in cold water, and melt at 107° .

Paradiazobenzoic acid and methyl alcohol yield methylparahydroxybenzoic acid, which melts at $183\text{--}184^{\circ}$, whilst orthodiazobenzoic acid yields only benzoic acid.

With ethyl alcohol, metadiazobenzoic acid yields a mixture of benzoic and ethylmetahydroxybenzoic acid. The products can be easily separated as the latter is almost insoluble in water; it forms white, crooked needles, melting at 137° .

Paradiazobenzoic acid with methyl alcohol yields benzoic and ethyl-parahydroxybenzoic acids, which can be separated as in the preceding case; the latter acid melts at 107°. Orthodiazobenzoic acid is completely converted into benzoic acid.

With phenol, metadiazobenzoic acid yields *metaphenoxybenzoic acid*; this crystallises from dilute alcohol in long, white needles, melting at 145°. It is almost insoluble in boiling water, but dissolves readily in alcohol and ether; it can be distilled in small quantities without decomposition. The barium salt, $(\text{OPh} \cdot \text{C}_6\text{H}_4 \cdot \text{COO})_2\text{Ba} + 3\frac{1}{2}\text{H}_2\text{O}$, crystallises in small, white, ill-defined leaves.

Paradiazobenzoic acid and phenol give paraphenoxybenzoic acid, which has already been described by Klepl (Abstr., 1884, 446). Orthodiazobenzoic acid yields hydroxydiphenylene ketone, orthophenoxybenzoic acid, and a new compound, which crystallises in white, shining needles, melting at 205°, and is tolerably readily soluble in hot water. This product seems to be isomeric with orthophenoxybenzoic acid.

Hydroxydiphenylene ketone melts at 96°, not 91° as stated by Richter (Abstr., 1884, 325).

Orthophenoxybenzoic acid is identical with the phenylsalicylic acid obtained by Graebe (this vol., p. 477).

The sulphate of orthotetrazodiphenic acid, $\text{C}_{12}\text{H}_6(\text{N}_2\text{SO}_4\text{H})_2(\text{COOH})_2$, a compound which is obtained from the sulphate of orthodiamidodiphenic acid by treating it with nitrous acid, when warmed with ethyl alcohol, yields aldehyde, sulphuric acid, nitrogen, and a new *diphenic acid*, $\text{C}_{12}\text{H}_6(\text{COOH})_2$ [$(\text{COOH})_2 = 3 : 3'$]. The latter is precipitated from its dilute ammoniacal solution in white, microscopic needles, and crystallises from boiling alcohol in small leaves. It is almost totally insoluble in cold water, and dissolves only sparingly in hot water, but more readily in hot alcohol, ether, and chloroform. The *barium salt* is tolerably readily soluble in water, from which it crystallises only slowly in nodular masses, having the formula $\text{C}_{12}\text{H}_6\text{O}_4\text{Ba} + 3\frac{1}{2}\text{H}_2\text{O}$. If the aqueous solution is evaporated down by boiling, the salt separates in needles which only contain $1\frac{1}{2}$ mol. H_2O . When the salt is subjected to dry distillation, it yields diphenyl (m. p. 70°) and barium carbonate. F. S. K.

Action of Potassium Ferrocyanide on Diazobenzene Nitrate. By M. LOCHER (*Ber.*, 21, 911—913).—The yellow, crystalline compound (m. p. = 150°) obtained, together with azobenzene and an oil, by Griess by the action of a cold saturated solution of potassium ferrocyanide on diazobenzene nitrate (this Journal, 1876, i, 932), when heated with aniline hydrochloride and aniline at 160°, yields an induline which is insoluble in alcohol. When reduced by the action of hot hydrochloric acid and tin, or by heating with concentrated hydriodic acid and amorphous phosphorus at 120—130°, Griess' compound is converted into aniline and paramidodiphenyl, and must therefore be regarded as benzeneazodiphenyl, $\text{Ph} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Ph}$. The *hydrazo*-derivative, $\text{C}_{18}\text{H}_{16}\text{N}_2$, obtained by treating its solution in absolute alcohol first with ammonia and then with hydrogen sulphide, crystallises in needles or thin scales, melts at 127°, and is readily converted into benzeneazodiphenyl

by exposure to the air and by distillation. Concentrated sulphuric acid dissolves it with a dark-red colour, which afterwards changes to green. When the hydrazo-derivative is boiled with acetic anhydride, the *acetyl*-derivative, $C_{18}H_{14}N_2Ac_2$, is formed; this crystallises in small, white needles, decomposes partially at 190° with the production of a yellow colour, and melts at $202-203^\circ$.

Under like conditions, potassium ferrocyanide reacts with diazo- α -naphthylamine (? naphthalene), and two compounds are obtained; one of these crystallises in dark-red, spherical aggregates, melts at about 200° , and seems to be azonaphthalene.

W. P. W.

Hydrazones. By E. FISCHER (*Ber.*, **21**, 984—988).—The name hydrazone is proposed for the compounds of hydrazine with aldehydes and ketones, and the term *osazone* for those compounds containing two neighbouring hydrazone-groups. Other compounds containing two hydrazone-groups may be named *dihydrazones*. Since phenylhydrazine is almost the only reagent employed, the word "phenyl" may usually be dispensed with.

The author gives the following reasons why the hydrazones must be considered as isomeric and not identical with the azo-compounds:—(1) Hydrazone-formation takes place equally well with a primary or with a secondary hydrazine, but in the latter case the formation of an azo-compound is excluded. (2) Most hydrazones regenerate the hydrazine bases when boiled with acids; only in isolated cases are indoles formed instead. (3) The hydrazone of acetaldehyde is isomeric with benzeneazoethane. Of the two formulæ for hydrazones, $R \cdot NH \cdot N : C =$ and $\langle \begin{smallmatrix} NH \\ NR \end{smallmatrix} \rangle C =$, the author considers the former as the most probable, and that the osazones are similarly constituted. In taking the melting point of a hydrazone, it should be borne in mind that many of them melt with decomposition, and constant melting points can only be obtained by raising the temperature as quickly as possible.

F. S. K.

Compounds of Phenylhydrazine with Sugars. By E. FISCHER (*Ber.*, **21**, 988—991).—The conversion of any known sugar into the crystalline and sparingly soluble osazone is the best method for recognising the former, or for isolating new compounds belonging to this class of substances.

By this method it was found that *phlorose*, the sugar obtained from phloridzin by Hesse (*Abstr.*, 1878, 851), is identical with dextrose. *Croco*se, a sugar prepared from saffron, also consists of dextrose, but it was not proved whether any other sugar is present or not. Formose, the product obtained from formaldehyde and calcium hydrate (Butlerow, *Compt. rend.*, **53**, 145; Loew, *Abstr.*, 1886, 609), is, according to the latter authority, a distinct compound, having the formula $C_6H_{12}O_6$. The only crystalline derivative of formose is the osazone, which, according to Loew, has the formula $C_{18}H_{22}N_4O_3$. The author finds that this osazone is a mixture of at least two, perhaps three or four osazones. One of these, $C_{18}H_{22}N_4O_4$, is the normal osazone of a

sugar, $C_6H_{12}O_6$; it was obtained in very slender, yellow needles, which began to soften at 130° , and melted completely at 144° . It is therefore impure, but the other compounds present are perhaps simply isomerides. It is comparatively readily soluble in hot water, and dissolves very readily in alcohol and ethyl acetate, far less readily in benzene.

A second osazone, which is sparingly soluble in ether and ethyl acetate, and can therefore be separated from the preceding compound by this means, gave results on analysis which agreed for the mean of the two formulæ $C_{17}H_{20}N_4O_3$ and $C_{18}H_{22}N_4O_4$.

A third osazone, which is only present in small quantities, was isolated. In melting point, which is above 204° , and its very sparing solubility in hot alcohol, it resembles phenylglucosazone and α -phenyl-acrosazone.

Methylenitan yields an osazone which has in general the same properties as the compound obtained from formose. Loew's statement (this vol., p. 572) that methylenitan does not yield an osazone, and is on that account quite different from formose; is therefore incorrect.

F. S. K.

Franceïns. By C. ISTRATI (*Compt. rend.*, **106**, 277—280).—Benzene and its chloro-, nitro-, and other derivatives yield a *franceïn* when heated with strong sulphuric acid (compare this vol., p. 259), the proportion of franceïn obtained increasing with the proportion of chlorine in the benzene-derivative. All the franceïns are soluble in strong sulphuric acid, and some are soluble in water. With two exceptions, they dissolve in alkalis and form neutral salts very soluble in water. They are all more or less soluble in alcohol, forming highly coloured and strongly dichroic solutions. They dye cotton, linen, and especially silk, with shades varying from rose colour to maroon. The depth of colour and the tinctorial power of the franceïns increase with the proportion of chlorine.

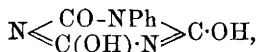
The franceïns from benzene, methylbenzene, and mono- and di-chlorobenzene are black, but they become redder and acquire a conchoidal fracture and a dark-green metallic lustre, as the proportion of chlorine increases.

The action of sulphuric acid on pentachlorobenzene yields two franceïns (*loc. cit.*). The first has a deep green metallic lustre, and dissolves in potash, methyl, ethyl, and amyl alcohols and glycerol, but is insoluble in water. Its solution shows intense red-green dichroism, and dyes silk a rose colour. The second is formed in much smaller quantity, and is soluble in warm water, but is almost insoluble in potash, and is much less soluble in alcohol than the first franceïn. It dyes silk a peach colour. The first franceïn forms salts which differ in their solubility in water and alcohol, and also in their dichroism. Both franceïns have the composition $C_{18}HCl_5O_6$, and seem to have the functions of a phenol and a diquinone.

C. H. B.

Phenylisocyanuric Acid : a Fourth Triphenylmelamine. By B. RATHKE (*Ber.*, **21**, 867—873).—When the triphenylamine previously described by the author (*Abstr.*, 1887, 662) is heated with

concentrated hydrochloric acid at 160—170°, it is converted, with elimination of aniline, into *phenylisocyanuric acid*,



this crystallises in flat needles, melts at 285—289° (uncorr.), and is readily soluble in hot water. The silver salt crystallises in lustrous, quadratic plates.

To the description previously given of the triphenylmelamine, $\text{NH} \begin{array}{c} \text{C(NPh)·NPh} \\ \diagup \quad \diagdown \\ \text{C(NPh)-NH} \end{array} \text{C:NH}$ (*loc. cit.*), the following is added. It melts at 221°, and crystallises in small prisms. The hydrochloride and sulphate are very readily soluble in water, the nitrate less so; a definite platinumchloride was not obtained. When heated with hydrochloric acid at 100—150°, or when heated with alcohol and a little ammonia at 150°, it is converted into normal triphenylmelamine, aniline, and diphenylmelamine, melting at 202—204°.

Fresh proof of the correctness of the formula usually assigned to normal triphenylmelamine was obtained by heating it with hydrochloric acid at 180°, when it yielded cyanuric acid, showing that the phenyl-groups were not in direct union with the ring. Hofmann's statement that normal triphenylmelamine is destitute of basic properties is incorrect. The salts are insoluble in water and very unstable; the *platinochloride*, $(\text{C}_{21}\text{H}_{18}\text{N}_6)_2 \cdot \text{H}_2\text{PtCl}_6$, crystallises in needles. When the platinochloride in alcoholic solution is treated with zinc-dust, it yields a new base crystallising in silvery, six-sided plates, and melting at 146°. A. J. G.

Dimethylanilinequinonimide. By J. FOGH (*Ber.*, 21, 887—890).—If paramidophenolsulphonic acid, made into a thin paste with water, is treated with chlorine until complete solution takes place (compare Hirsch, *Abstr.*, 1887, 834), and the excess of chlorine is removed by the addition of small quantities of the acid until no more is dissolved, a solution of quinonechlorimidesulphonic acid is obtained, which on the addition of dimethylaniline becomes bluish-violet owing to the formation of the *dimethylaniline*-derivative of quinonimidesulphonic acid, $\text{O} \begin{array}{c} -\text{C}_6\text{H}_3(\text{SO}_3\text{H}) \\ \diagup \quad \diagdown \\ \text{N}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2) \end{array} \text{C}$. This separates in flocks having a bronze lustre, and consisting of microscopic needles which contain $\frac{1}{2}$ mol. H_2O , are practically insoluble in cold water, ether, and benzene, and sparingly soluble in hot alcohol, but are readily soluble in aqueous alkalis, yielding intensely blue solutions from which acids precipitate the compound unchanged. The compound dissolves in concentrated sulphuric acid with a cherry-red colour, is decolorised by boiling with dilute mineral acids, and when heated at 100° or treated with reducing agents, is converted into a leuco-derivative. It is probably identical with the compound obtained by Schmitt and Andresen from trichloroquinonechlorimide and dimethylaniline (*Abstr.*, 1882, 400).

Dimethylanilinequinonimide (phenol-blue) can be prepared by adding dimethylaniline (50 grams) to a concentrated aqueous solution

of oxalic acid (50 grams) containing quinonechlorimide (30 grams) in suspension, and shaking the mixture until complete solution occurs. The blue colour of the solution then changes to green, and green flocks of the oxalate separate, from which the dimethylaniline-derivative can be obtained by treatment with cold aqueous soda. It is identical with the compound obtained by Möhlau from dimethyl-phenylene-green (Abstr., 1886, 146).

Quinonechlorimide is best prepared by reducing 100 grams of paranitrophenol with 100 grams of tin and 500 to 600 grams of concentrated hydrochloric acid, filtering, diluting to 1 litre, and treating the solution, further diluted with four times its volume of water, and cooled to 5°, in small quantities at a time with bleaching-powder solution until both the precipitate and solution are coloured a pure yellow; the precipitate then only requires to be washed. The yield amounts to 70—80 per cent. of that theoretically possible.

W. P. W.

Base from Bromacetophenone and Acetamide. By M. LEWY (*Ber.*, 21, 924—931; compare this vol., p. 55).—The base from bromacetophenone and acetamide yields benzoic acid when oxidised with a very dilute permanganate solution. Fuming nitric acid converts it into a *nitro*-derivative, $\text{NO}_2 \cdot \text{C}_{10}\text{H}_8\text{NO}$, which crystallises in long, bright-yellow needles, melts at 156—157°, is readily soluble in hot alcohol and benzene, insoluble in water, and on oxidation with dilute permanganate solution yields paranitrobenzoic acid. When treated with stannous chloride and hydrochloric acid, it is reduced to the *amido*-derivative, $\text{NH}_2 \cdot \text{C}_{10}\text{H}_8\text{NO}$; this crystallises in long, lustrous, colourless needles, melts at 114—115°, is readily soluble in alcohol, ether, and hot water, and readily yields a diazo-compound, which forms with dimethylaniline a violet, with resorcinol a yellow, and with β -naphthol a red colouring matter.

The *tetrahydro*-base, $\text{C}_{10}\text{H}_{13}\text{NO}$, is obtained by gradually adding sodium in large excess to a boiling alcoholic solution of the acetamide base. It is a colourless oil of repulsive odour, boils at 242—251°, and is readily soluble in alcohol, ether, and concentrated acids. The *benzoyl*-derivative, $\text{C}_{10}\text{H}_{12}\text{BzNO}$, crystallises in small, white, concentrically grouped needles, melts at 140°, and is readily soluble in hot alcohol, ether, and benzene.

The acetamide-base does not react with hydroxylamine, phenylhydrazine, or phosphorus pentachloride, and is not decomposed on distillation either with soda-lime or with zinc-dust. When heated with hydriodic acid and amorphous phosphorus for 12 hours at 210°, it is converted into a hydrocarbon, $\text{C}_{16}\text{H}_{18}$, which boils at 270—280°, and seems to be identical with a compound obtained by Graebe from acetophenone under similar conditions (this Journal, 1875, 457). The author regards the acetamide-base as a

methylphenyloxazole, and ascribes to it the formula $\text{< } \begin{smallmatrix} \text{N}:\text{CMe} \\ \text{CH}:\text{CPh} \end{smallmatrix} \text{>O}$,

and to its tetrahydro-derivative the formula $\text{< } \begin{smallmatrix} \text{NH}\cdot\text{CHMe} \\ \text{CH}_2\cdot\text{CHPh} \end{smallmatrix} \text{>O}$.

W. P. W.

Action of Phosphorus Pentachloride on Anilic Acids of Bibasic Acids. By R. ANSCHÜTZ (*Ber.*, **21**, 957).—Anilic acids (this vol., pp. 277 and 367) can be readily converted into the corresponding *anils* by the action of an equivalent quantity of phosphorus pentachloride on the acid suspended in chloroform.

Succinanil, succinparatolil, succinorthotolil, and succin- α -naphthil, &c., were prepared by this method. Fumaranilic acid yields a product, the formula of which agrees with that of monochloro-succinanil. F. S. K.

Itaconanilic Acid. By R. ANSCHÜTZ and F. REUTER (*Ber.*, **21**, 958—959).—The authors have shown that the itaconanilic acid which they obtained (this vol., p. 277) is different from that prepared by Gottlieb (*Annalen*, **77**) and by Michael. In this article they discuss the formula of Gottlieb's and Michael's acid, and give $\text{COOH}\cdot\text{CH}<\begin{smallmatrix} \text{CH}_2\cdot\text{NPh} \\ \text{CH}_2\cdot\text{CO} \end{smallmatrix}>$ as the most probable. F. S. K.

Chloronitrobenzoic Acids. By A. CLAUS and H. KURZ (*J. pr. Chem.* [2], **37**, 196—201).—The substances described in this paper have been prepared from the corresponding amido-compounds by Sandmeyer's reaction.

Parachlorometanitrobenzonitrile, $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CN}$, dissolves readily in alcohol, ether, chloroform, and hot water, from which it crystallises in colourless needles, melting at $100\text{--}101^\circ$ (uncorr.). When boiled with dilute sulphuric acid, it forms *parachlormetanitrobenzoic acid*, which crystallises in pale-yellow needles, melting at $178\text{--}179^\circ$ (uncorr.).

Parachlororthonitrobenzonitrile dissolves readily in alcohol, ether, and hot water. It forms colourless needles, melting at 98° (uncorr.). *Parachlororthonitrobenzoic acid* crystallises from hot water in long, colourless needles, melting at 139° (uncorr.). The sodium salt (6 mols. H_2O) is very soluble in water, from which it crystallises in flat needles. The potassium, copper, barium, ammonium, calcium, and silver salts are described.

Metachloroparanitrobenzonitrile crystallises from alcohol, ether, and hot water in colourless needles, melting at 87° (uncorr.). *Metachloroparanitrobenzoic acid* forms long, white needles, melting at $185\text{--}186^\circ$ (uncorr.), and is very soluble in alcohol, ether, chloroform, and hot water. The ammonium, silver, barium (2 mols. H_2O), and calcium (2 mols. H_2O) salts are all soluble in hot water, and crystallise in colourless needles. The ammonium salt dissociates at 100° .

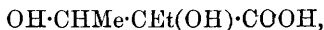
G. T. M.

Hydroxy- β -isodurylic Acid. By C. KROHN (*Ber.*, **21**, 884—886).—*Hydroxy- β -isodurylic acid*, $\text{OH}\cdot\text{C}_6\text{HMe}_3\cdot\text{COOH}$ [$\text{Me}_3 : \text{OH} : \text{COOH} = 1 : 3 : 4 : 6 : 5$], is obtained when the sodium-derivative of pseudocumenol is heated with excess of liquid carbonic anhydride at 170 to 180° . It crystallises in snow-white needles, melts at 181° , and at a slightly higher temperature decomposes into pseudocumenol and carbonic anhydride. It is readily soluble in ether, sparingly in the other organic solvents; the alcoholic solution gives a permanent blue coloration with ferric chloride. When treated with a mixture of acetic and nitric acids, it yields Auwers' nitropseudocumenol nitrate

(Abstr., 1885, 380). When a solution of the acid in concentrated sulphuric acid is heated at 50—70°, carbonic anhydride is abundantly evolved, and Reuter's pseudocumenolsulphonic acid (Abstr., 1878, 413) is formed. A. J. G.

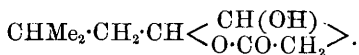
Oxidation of Unsaturated Acids. By R. FITTIG (*Ber.*, 21, 919—921).—The oxidation of the following unsaturated acids was effected by gradually adding the equivalent quantity (1 mol. to 1 mol. of the acid) of a 2 per cent. permanganate solution to a very dilute aqueous solution of the alkaline salt of the acid cooled to 0°. The yield is good, and the products can be purified with little difficulty.

The α - β -unsaturated acids yield dihydroxy-acids, which do not undergo change when boiled with dilute hydrochloric acid. Cinnamic acid, for example, is converted into phenylglyceric acid together with small quantities of benzaldehyde and oxalic acid, and ethylcrotonic acid is oxidised to the dihydroxy-acid,



which crystallises well, melts at 95—96°, and is not identical with How's hexeric acid obtained in very small quantity in the decomposition of the dibromide of ethylcrotonic acid.

The β - γ -acids yield dihydroxy-acids which, when warmed with dilute hydrochloric acid, readily undergo conversion into the corresponding hydroxy-lactones. Thus, isophenylcrotonic acid forms the beautifully crystalline *phenylhydroxybutyrolactone*, $\text{OH}\cdot\text{CH}<\begin{smallmatrix} \text{CH}_2\cdot\text{CO} \\ \text{CHPh} \end{smallmatrix}>\text{O}$, + $\frac{1}{2}\text{H}_2\text{O}$, which melts at 76—77°, or, when anhydrous, at 86—87°. The corresponding *phenyldihydroxybutyric acid*, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{COOH}$, forms large crystals, and melts at 116°, with decomposition into the hydroxy-lactone. Isocytlenic acid, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{COOH}$, obtained by the distillation of isobutylparaconic acid, is in like manner converted into the liquid hydroxy-lactone,



The γ - δ -acids, as, for example, cinnamenylpropionic acid and hydro-sorbic acid, also yield hydroxy-lactones, which differ, however, in many respects from those obtained from the β - γ -acids. The research, which has been carried on in conjunction with the author's pupils, is being continued. W. P. W.

Iodophenolsulphonic Acids. By F. KEHRMANN (*J. pr. Chem.* [2], 37, 9—14).—When iodine (1 mol.), in the form of a mixture of potassium iodide and iodate, is added little by little to potassium paraphenolsulphonate (1 mol.) dissolved in excess of dilute hydrochloric or sulphuric acid, iodine at first separates, but is quickly re-absorbed, and after a short time the liquid crystallises to a dense mass of long, thin prisms of the formula $\text{C}_6\text{H}_3\text{I}_2\text{O}\cdot\text{SO}_3\text{K} + 2\text{H}_2\text{O}$. This salt begins to decompose at 270° without melting. The barium salt, $(\text{C}_6\text{H}_3\text{I}_2\text{O}\cdot\text{SO}_3)_2\text{Ba} + 3\text{H}_2\text{O}$, is only slightly soluble in cold water from which it crystallises in white, glistening needles. The copper salt

forms pale green, monoclinic prisms. The anhydrous free acid melts at 120° , and decomposes with separation of iodine at 190° . It dissolves readily in water from which it is precipitated by hydrochloric or sulphuric acid. It probably has the constitution $[\text{HO} : \text{I}_2 : \text{SO}_3\text{H} = 1 : 2 : 6 : 4]$.

The mother-liquor on evaporation yields a considerable quantity of unchanged potassium paraphenolsulphonate, and an amount insufficient for analysis of a substance containing iodine, and crystallising in gleaming scales. G. T. M.

Iodophenolsulphonic Acids. By E. OSTERMAYER (*J. pr. Chem.* [2], 37, 213—216).—If paraphenolsulphonic acid (1 mol.) is treated with iodine (1 mol.) in the way described by Kehrmann (this vol., p. 595), besides the chief product, diiodophenolsulphonic acid, a compound is produced which appears to be a moniodosulphonic acid. This acid forms thick, colourless crystals belonging to the rhombic system, and differs from the diiodosulphonic acid by its barium and calcium salts dissolving readily in water. The diiodosulphonic acid forms a zinc salt, $(\text{OH} \cdot \text{C}_6\text{H}_4\text{I}_2 \cdot \text{SO}_3)_2\text{Zn} + 6\text{OH}_2$, which crystallises in long, colourless needles. The paper is mainly on the question of priority between the author and Kehrmann (*loc. cit.*). G. T. M.

New Synthesis of Tetraphenylethylene. By J. H. ZIEGLER (*Ber.*, 21, 779—781).—When equivalent quantities of sulphur and diphenylmethane are heated together, the former begins to dissolve at 110° , and the solution is complete at 150° ; the scarcely yellow solution yields crystals of unaltered sulphur on cooling. On raising the temperature, the liquid slowly darkens at 200° , and an evolution of hydrogen sulphide begins; the reaction requires 10 hours' heating at 240 — 290° for completion. The residue consists mainly of tetraphenylethylene, and can be purified by treatment with ether in which unaltered diphenylmethane, &c., dissolve. The yield is about 75 per cent. of the diphenylmethane employed. A. J. G.

Action of Chlorine on α - and β -Naphthol. By P. T. CLEVE (*Ber.*, 21, 891—896).—*Dichloro- α -naphthol*, $\text{C}_{10}\text{H}_7\text{Cl}_2 \cdot \text{OH}$ (probably $\text{OH} : \text{Cl} : \text{Cl} = 1 : 2 : 4$), is obtained, together with chloro- α -naphthol, by the action of chlorine on a cold solution of α -naphthol in acetic acid. It crystallises from alcohol, chloroform, and benzene in silky needles melting at 106° , and from acetic acid in prisms having the composition $\text{C}_{10}\text{H}_7\text{Cl}_2 \cdot \text{OH} + \text{C}_2\text{H}_4\text{O}_2$; these lose the associated acetic acid completely at 40 — 50° . When heated at 170 — 180° , it loses hydrogen chloride, and is converted into a compound which probably has the composition $\text{C}_{20}\text{H}_{10}\text{Cl}_2\text{O}_2$, does not melt at 275° , and is insoluble in all the ordinary solvents. On oxidation with dilute nitric acid, dichloro- α -naphthol yields phthalic acid and a quinone-like compound crystallising in yellow needles, whilst *chloronaphthaquinone*, $\text{C}_{10}\text{H}_5\text{ClO}_2$, is formed when it is treated with chromic acid in acetic acid solution; this crystallises in lustrous, golden-yellow needles, melts at 116° , is soluble in alcohol, and yields an *anilide*, $\text{C}_{10}\text{H}_4\text{ClO}_2 \cdot \text{NHPh}$, which forms sparingly soluble, purple-red crystals

and melts at 202—203° (compare Knapp and Schultz, Abstr., 1882, 510; Claus, *Ber.*, **18**, 2929). When treated with phosphorus pentachloride, dichloro- α -naphthol is converted into a trichloronaphthalene ($= 1 : 2 : 4?$), which crystallises in needles and melts at 92°.

Chloro- α -naphthol (probably $\text{OH} : \text{Cl} = 1 : 2$), owing to its great solubility in the ordinary solvents, could only be crystallised from light petroleum. It could not, however, be obtained pure either by distillation or by fractional crystallisation; the impure crystals melted at about 54°. When treated in acetic acid solution with chlorine, it is converted into the dichloro-derivative, whilst phosphorus pentachloride reacts with it to form the above trichloronaphthalene.

Chloro- β -naphthol, $\text{C}_{10}\text{H}_7\text{Cl}\cdot\text{OH}$, is obtained under like conditions from β -naphthol. It crystallises from chloroform in monoclinic forms, $a : b : c = 1.9600 : 1 : 1.9562$; $\beta = 66^\circ 54'$; observed faces, 0P , $\infty\text{P}\infty$, $+\text{P}\infty$, $-\text{P}\infty$, ∞P , melts at 70° , and is readily soluble in alcohol, benzene, chloroform, acetic acid, and boiling light petroleum; it is also soluble in hot water from which it crystallises in talc-like scales. When heated with phosphorus pentachloride, it yields a dichloronaphthalene melting at 34° (compare Abstr., 1887, 961), and also the orthophosphate, $(\text{C}_{10}\text{H}_6\text{ClO})_3\text{PO}$, which crystallises from alcohol in microscopic needles, melts at 152° , is insoluble in water and only very sparingly soluble in hot alcohol.

W. P. W.

Investigation of the Second Van't Hoff Hypothesis. By K. AUWERS and V. MEYER (*Ber.*, **21**, 784—817).—The second hypothesis which Van't Hoff deduced from his arrangement of atoms in space is that two carbon-atoms united by a single affinity are free to rotate, the axis of rotation being the bond of union, and that isomerism is only possible for those substances of the type $\text{C}\equiv\text{C}\equiv$ which cannot by rotation round the common axis be converted into the same form. As the existence of the two isomeric dioximes of benzil, discovered by V. Meyer and H. Goldschmidt, would, if for both the formula $\text{Ph}\cdot\text{C}(\text{NOH})\cdot\text{C}(\text{NOH})\cdot\text{Ph}$ were established, be in direct contradiction to the above hypothesis, the present paper contains a series of investigations by which the authors have sought to ascertain whether the composition of the above two compounds is identical.

The preparation of the dioximes is that formerly described. By treating benzil in alcoholic solution with hydroxylamine hydrochloride, the α -dioxime is formed, and from this the β -dioxime may be easily obtained by simply heating with three times its weight of absolute alcohol at 170 — 190° for some hours. The α -dioxime separates from alcohol as a white, crystalline powder, melting with decomposition at 237° , insoluble in water, and nearly insoluble in acetic acid, ether, and alcohol, of which the last dissolves 0.05 part per 100 at 17° . The β -dioxime crystallises from alcohol in slender needles melting with decomposition at 206 — 207° , slightly soluble in water, and easily soluble in acetic acid, ether, and alcohol, of which the last dissolves 15.26 parts per 100 at 17° . Of the two forms, the latter is the more stable into which the first is readily converted, but change in the opposite direction never takes place. Thus the α - is converted into the β -dioxime when it is heated with alcohol at 170° , or with water at

200°, also when it is treated with acetic chloride or with hydrogen chloride in acetic acid solution. Both are true derivatives of benzil, as both yield benzil and hydroxylamine hydrochloride when heated with concentrated hydrogen chloride in a sealed tube at 100°. The change takes place somewhat less readily with the β - than with the α -compound.

The non-existence of true nitroso-groupings in either compound is shown by each yielding a diacetyl-derivative when treated with acetic anhydride. α -Diacetyldiphenylglyoxime melts at 147—148°, is insoluble in water, and sparingly soluble in alcohol and acetic acid. β -Diacetyldiphenylglyoxime melts at 124—125°, and is easily soluble in alcohol and acetic acid, from the hot solutions of which it crystallises in fine needles. On treatment with alkalis, both derivatives yield the oximes from which they were prepared.

To further remove all doubt as to the possibility of merely physical isomerism, and to prove that the oximes are not only different from one another, but yield different derivatives, reconvertible into their respective oximes, the propionic and isobutyric derivatives were also prepared.

Dipropionyldiphenylglyoxime.—The α -derivative is easily soluble in alcohol, acetic acid and ether, and crystallises in thin scales melting at 103—104°; the β -derivative is slightly soluble in alcohol and acetic acid, soluble in ether, crystallises in oblique prisms, and melts at 121°. *Diisobutyryldiphenylglyoxime*.—The α -derivative is easily soluble in alcohol, ether, and acetic acid, and crystallises in flat needles melting at 121—122°; the β -derivative is very soluble in alcohol, ether, and acetic acid, crystallises in quadratic prisms melting at 88—89°, below which temperature the substance begins to sublime.

The two oximes were oxidised by means of potassium ferricyanide, and both were found to give the same oxidation-product—that described by Koreff (Abstr., 1886, 363). By reduction of this product with hydriodic acid, pure dibenzyl is obtained, thus proving the presence of the Ph·C·C·Ph-group in the original compounds and the oxidation-product, and confirming Koreff's view of the constitution of the latter. Hence it is a polymeride and not, as Gabriel (Abstr., 1886, 693) assumed, an isomeride of phenyl cyanate, which it furnishes on strongly heating. An attempt by reduction to again obtain either of the oximes failed, but a *dioxime-anhydride*, $\langle \begin{smallmatrix} \text{C}^{\text{Ph}\cdot\text{N}} \\ \text{C}^{\text{Ph}\cdot\text{N}} \end{smallmatrix} \rangle \text{O}$, melting at 94° was obtained.

In order to ascertain whether there was any tendency towards the formation of the group $\langle \text{C} \rangle \text{N}\cdot\text{OH}$, attempts were made to prepare compounds containing this group from stilbene bromide by treatment with hydroxylamine and nitrous acid. These, however, failed to yield any product of an oxime character, as also did the treatment with amyl nitrite and sodium alcoholate. Isobenzil, $\text{Ph}\cdot\text{C}\langle \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} \rangle \text{C}\cdot\text{Ph}$, when heated with hydroxylamine hydrochloride and absolute alcohol at 140—150°, did appear to yield the β -dioxime, but under the conditions of the experiment it must be assumed that the isobenzil is converted into benzil, and that the latter yields the dioxime.

Both oximes, when heated in sealed tubes with water for some hours at a temperature above 200° , yield one and the same anhydride, the dioxime-anhydride melting at 94° before mentioned. It crystallises in flat needles, moderately soluble in cold alcohol, easily soluble in ether and acetic acid. As the formation of the anhydride takes place at a temperature above that at which the α - is converted into the β -dioxime, a direct formation from the α -derivative does not occur and has not yet been found possible. The anhydride is also obtained on heating the diacetyl-derivative with alcohol at 170 – 190° . It is a stable substance, can be heated with alkalis for hours, or with hydrogen chloride in a sealed tube, or even with hydrogen iodide for some time without change. Only on heating for at least 10 hours with hydrogen iodide at 230° does it yield dibenzyl. The formation of only one and the same anhydride from the isomeric dioximes is similar to the formation of the same anhydride from fumaric and maleic acids.

In order to prove that the compound obtained by Beckmann (Abstr., 1887, 827), by heating the dioxime with sulphuric acid, was no anhydride, it was prepared and examined by treatment with hydrogen iodide. It gave not dibenzyl but benzoic acid, showing that intramolecular change had undoubtedly taken place. The above compound could only be obtained from the α -dioxime.

The determination of the molecular weights by Raoult's method, which has been already described (this vol., pp. 407, 408) gave practically the same value for each dioxime. The α -compound gave 333, the β -compound 320—the theoretical value being 324.

By these results, then, the identity of the two dioximes in chemical composition has been established, and it is therefore thought necessary that the second Van't Hoff hypothesis must in so far be altered as to admit of some cases in which free rotation round the axis cannot take place, as otherwise no explanation of the isomerism is possible.

H. C.

β -Tetrahydronaphthylamine. By E. BAMBERGER and R. MÜLLER (*Ber.*, 21, 847–860).— β -Tetrahydronaphthylamine (this vol., p. 159) is best prepared by allowing a boiling solution of β -naphthylamine (15 grams) in absolute amyl alcohol (170–180 grams) to flow in a continual stream on to sodium (12 grams) contained in a flask connected with a good condenser; the mixture is then heated so that the temperature does not fall below the boiling point of the amyl alcohol until the whole of the sodium has dissolved. The product is poured into water and the upper layer separated. The bases are converted into hydrochlorides, dissolved in hot water, mixed with excess of soda, and the separated bases dissolved in ether. The ethereal solution is well cooled, and a stream of steam saturated with carbonic anhydride is passed into the liquid, when β -tetrahydronaphthylamine carbonate is completely precipitated in a nearly pure condition, whilst the unaltered β -naphthylamine remains in solution. Dihydronaphthalene is formed as a bye-product in the reaction. Tetrahydronaphthylamine is a colourless, slightly viscid liquid, turning brown if exposed to the air for some time, and has an intense ammoniacal, piperidine-like odour; it boils at 162° under 36 mm. pressure, and at 249.5° under 710 mm. (corr.), in the last case with slight decomposition;

sp. gr. 1.031 at 16°. It is but little soluble in water, readily soluble in the organic solvents. It is one of the strongest organic bases, eagerly absorbs carbonic anhydride from the air, has a strongly alkaline reaction, and does not yield colouring matters with diazo-compounds; in all these respects differing markedly from β -naphthylamine. When oxidised, it yields a carboxyphenylpropionic acid (1 : 2), whilst β -naphthylamine gives phthalic acid.

The salts of β -tetrahydronaphthylamine are all more or less soluble in water, and crystallise well. The *carbonate*, $(C_{10}H_{11}\cdot NH_2)_2\cdot H_2CO_3$, forms lustrous, white needles; the *hydrogen carbonate*,



is a white, granulo-crystalline powder; the *hydrochloride*,



forms silvery-white tables, and melts at 237°; the *sulphate* forms lustrous, white prisms; the *dichromate* crystallises in orange-yellow prisms; the *platinochloride*, $(C_{10}H_{11}\cdot NH_2)_2\cdot H_2PtCl_6$, forms satiny, orange-yellow prisms; the *aurochloride* forms golden-yellow needles; the *mercuochloride* is very characteristic—it is precipitated in silky, interlaced needles converted on recrystallisation from boiling water into inch-long prisms of vitreous lustre melting at 241.5°. The *hydrobromide*, *picrate*, and *ferrocyanide* are also described. The *acetyl-derivative*, $C_{10}H_{11}\cdot NHAc$, melts at 107.5°, the *benzoyl-derivative* at 150—151°.

The *nitrite*, $C_{10}H_{11}\cdot NH_2\cdot HNO_3$, is prepared by passing nitrous gases into a well-cooled solution of the base in dry ether; it crystallises in tufts of long, silky needles or in short, strongly-refractive prisms, and melts at 160° with decomposition. It is characterised by the most extraordinary stability; its aqueous solution can be boiled for days without the least trace of decomposition: from this cause the authors were not able to prepare β -tetrahydronaphthol.

β -Tetrahydronaphthylamine tetrahydronaphthylthiocarbamate (*loc. cit.*) forms long, lustrous needles and melts at 142°. *Di- β -tetrahydronaphthylthiocarbamide*, $CS(NH\cdot C_{10}H_{11})_2$, prepared by boiling the preceding compound with alcohol, crystallises in stellate groups of lustrous, white needles, and melts at 161° with decomposition.

β -Tetrahydronaphthylphenylcarbamide, $NHPh\cdot CO\cdot NH\cdot C_{10}H_{11}$, prepared by the action of phenyl cyanate on the tetrahydro-base, crystallises in concentrically-grouped, long, silky needles, and melts at 166.5°.

A. J. G.

Bases from Dinaphthylthiocarbamide. By F. EVERS (*Ber.*, 21, 962—977).—Numerous experimenters have shown that ethereal salts, the constitution of which is $NH\cdot C(NH_2)\cdot SR$, are formed by the action of haloid alkyl-derivatives on thiocarbamides.

Methyl α -naphthylimidonaphthylthiocarbamate,



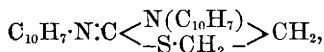
is obtained by acting on α -naphthylthiocarbamide with methyl iodide and treating the product with soda; it crystallises in colourless, flat prisms melting at 136°, is almost insoluble in cold alcohol, dis-

solves slowly in hot alcohol and ether, and is very stable. The *hydriodide*, $C_{22}H_{18}N_2S \cdot HI$, forms small, colourless crystals which melt at 174° and become yellow and insoluble on exposure to the light. The *platinochloride*, $(C_{22}H_{18}N_2S)_2 \cdot H_2PtCl_6$, is a yellow, crystalline powder, sparingly soluble in hot water and hot alcohol; it melts at 202° with decomposition. On heating the base, it yields α -carbodinaphthylimide and mercaptan, and when heated with alcoholic potash, α -dinaphthylcarbamide is obtained.

Ethyl α -naphthylimidonaphthylthiocarbamate, obtained in a similar manner to the methyl salt, forms large, prismatic crystals which melt at 98° , and are only sparingly soluble in hot alcohol. The *hydriodide* crystallises in clusters of colourless needles melting at 157° ; it is very sparingly soluble in hot water, and turns yellow on exposure to the light. The *platinochloride*, $(C_{23}H_{20}N_2S)_2 \cdot H_2PtCl_6$, forms small, yellow needles. The behaviour of this base towards alkalis, and on heating, is similar to that of the methyl-derivative.

Propyl α -naphthylimidonaphthylthiocarbamate crystallises in large, nacreous leaves melting at 95° . The *hydriodide* forms fine, shining needles which melt at 97° , and are very sparingly soluble in water even on addition of hydrochloric acid.

Ethylene α -naphthylimidonaphthylthiocarbamate,



crystallises in groups of concentric, colourless needles melting at 139° ; it dissolves slowly, but to a considerable extent in alcohol. The *platinochloride*, $(C_{23}H_{16}N_2S)_2 \cdot H_2PtCl_6$, is a yellow, crystalline powder which dissolves in a large quantity of hot water or alcohol, and decomposes when heated above 200° .

Methyl β -naphthylimidonaphthylthiocarbamate, crystallises in clusters of small needles melting at 110° ; it is very readily soluble in warm alcohol and ether. This compound is very unstable. The *platinochloride* crystallises in stellate forms which decompose above 150° without melting.

Ethyl β -naphthylimidonaphthylthiocarbamate forms shining, silky needles melting at 106° , and is less stable than the methyl-derivative. The *platinochloride* forms small, yellow crystals which decompose above 155° without melting.

Propyl β -naphthylimidonaphthylthiocarbamate crystallises in very small concentric needles which melt at 65 – 66° , and are readily decomposed. The *platinochloride* is a yellow, crystalline compound which decomposes above 120° without melting.

Ethylene β -naphthylimidonaphthylthiocarbamate crystallises from hot alcohol in silvery leaves melting at 172° . This base is tolerably stable, but turns reddish on exposure to the light. The *platinochloride*, $(C_{23}H_{18}N_2S)_2 \cdot H_2PtCl_6$, is a yellow, crystalline powder which decomposes above 146° without melting.

When the α -methyl base, described above, is heated with absolute alcoholic ammonia, α -dinaphthylguanidine is produced. α -*Tri-naphthylguanidine*, $C_{10}H_7 \cdot N : C(NH \cdot C_{10}H_7)_2$, is produced by heating the α -methyl base with α -naphthylamine in alcoholic solution; it forms

colourless, flat, needle-shaped crystals, melts at 178° , is insoluble in water, and only sparingly soluble in dilute acids, but dissolves in considerable quantities in hot alcohol, although slowly.

Methyl α -naphthylthiocarbamate, $C_{10}H_7 \cdot NH \cdot COSMe$, is formed by heating the α -methyl base with dilute sulphuric acid; it crystallises in groups of small, colourless needles melting at 122° , and dissolves readily in dilute alcohol, ether, and benzene, but is insoluble in water, dilute acids, and dilute alkalis. When heated with alcoholic ammonia, it yields α -mononaphthylcarbamide.

Ethylene α -naphthylthiocarbamate, $CO \langle \begin{smallmatrix} N(C_{10}H_7) \\ -S \cdot CH_2- \end{smallmatrix} \rangle CH_2$, is obtained when the α -ethylene base is heated with dilute hydrochloric acid; it crystallises in groups of small, almost colourless needles melting at 102° .

Methyl α -naphthylthiocarbamate, $C_{10}H_7 \cdot NH \cdot CSSMe$, is produced when the α -methyl base is heated with carbon bisulphide; it crystallises in small needles which melt at 185° , and dissolves tolerably readily in hot alcohol or ether, but is insoluble in water and dilute acids.

Ethylene α -naphthylthiocarbamate, $CS \langle \begin{smallmatrix} N(C_{10}H_7) \\ -S \cdot CH_2- \end{smallmatrix} \rangle CH_2$, crystallises from alcohol in narceous leaves melting at 198 – 199° ; it is insoluble in dilute acids and alkalis.

α -Dinaphthylparabanic acid, $CO \langle \begin{smallmatrix} N(C_{10}H_7) \cdot CO \\ N(C_{10}H_7) \cdot CO \end{smallmatrix} \rangle$, is obtained by treating the methyl base with cyanogen-gas in alcoholic solution; it crystallises in needles which melt at 246° and dissolve slowly, but to a considerable extent, in hot alcohol; it is sparingly soluble in ether, but insoluble in water and dilute acids. When treated with alcoholic potash, it yields carbonic anhydride, oxalic acid, and α -naphthylamine.

α -Dinaphthylthiohydantoïn, $C_{10}H_7 \cdot N \cdot C \langle \begin{smallmatrix} N(C_{10}H_7) \\ -S \cdot CH_2- \end{smallmatrix} \rangle CO$, is formed by the action of monochloroacetic acid on α -dinaphthylthiocarbamide; it crystallises in shining, yellow leaves, melts at 176° , is insoluble in water, but dissolves to a considerable extent, although slowly, in hot alcohol.

β -Dinaphthylthiohydantoïn resembles the preceding compound, and melts at 174° .

Ethyl, propyl, and allyl phenyldithiocarbamates all yield phenyldithiocarbamide glycolide when treated with monochloroacetic acid; similarly the ethereal salts of ortho- and para-tolyldithiocarbamic acid yield the corresponding tolyldithiocarbamide glycolide. Ethylene phenyldithiocarbamate yields thioglycollic acid and ethylene phenyldithiocarbamate by a similar treatment, and the ethylene ethereal salts of α -naphthyl-, ortho- and para-tolyldithiocarbamic acid behave in the same way.

F. S. K.

Dichlor- α -naphthaquinonesulphonic Acid. By A. CLAUS and SCHONEVELD VAN DER CLOET (*J. pr. Chem.* [2], **37**, 181–196).—The sodium dichlor- α -naphthaquinonesulphonate is prepared by treating 100 grams of sodium dinitro- α -naphtholsulphonate with 3 litres of hydrochloric acid (sp. gr. 1.09) and mixing the resulting pulp with

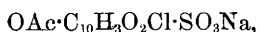
100 grams of sodium chlorate. After one day, the yellow solution is evaporated, and then deposits a bright-yellow, crystalline powder of the composition $C_{10}H_3O_2Cl_2 \cdot SO_3Na$. The acid is obtained by carefully decomposing the barium-salt with sulphuric acid. It dissolves readily in water and alcohol, and crystallises from hot hydrochloric acid in glistening yellow plates melting at 229° (uncorr.). The sodium salt is only slightly soluble in water, and crystallises from alcohol in yellow scales. With acid potassium sulphate, it forms a double salt of an intense yellow colour. The barium, calcium, lead, and silver salts are all anhydrous, and but slightly soluble in water.

When a solution of dichlor- α -naphthaquinonesulphonic acid is boiled with zinc and hydrochloric acid, the solution first becomes violet and eventually colourless. The violet solution gives with barium chloride a pale-red precipitate containing 18.19 per cent. of barium. It is probably the unstable quinol compound.

Dichlor- α -naphthaquinonesulphonic acid, like dichlor- α -naphthaquinone, when boiled with potash or soda, readily exchanges one of its atoms of chlorine for hydroxyl. *Hydroxychlor- α -naphthaquinonesulphonic acid*, $OH \cdot C_{10}H_3O_2Cl \cdot SO_3H$, is very soluble in water, slightly soluble in alcohol, but insoluble in ether and chloroform. After recrystallisation from hot hydrochloric acid, it melts at 211° (uncorr.) with decomposition. Its aqueous solution gives a dark red coloration with ferric chloride. Those salts in which only the hydrogen of the sulphonic acid-group is displaced by a metal are yellowish-red, whilst those in which the hydrogen of the hydroxyl is also displaced, are dark red. The sodium salt, $(ONa \cdot C_{10}H_3O_2Cl \cdot SO_3Na + 2H_2O)$, is readily dissolved by water, but is only slightly soluble in alcohol. The barium salt, $C_{10}H_3O_2ClSO_3Ba + 2H_2O$, crystallises from hot water in microscopic needles. The silver salt, $C_{10}H_3O_2Cl(OAg) \cdot SO_3Ag + H_2O$, is a heavy crystalline powder decomposed by heating to 170° .

By treating dichlor- α -naphthaquinone sodium sulphonate with potash and a large excess of phenol, *sodium phenoxychlor- α -naphthaquinonesulphonate*, $OPh \cdot C_{10}H_3O_2Cl \cdot SO_3Na + PhOH$, is obtained in the form of dark-yellow needles. The free acid melts with decomposition at 121° (uncorr.). The barium salt, $(OPh \cdot C_{10}H_3O_2Cl \cdot SO_3)_2Ba + 2PhOH$, crystallises from hot water in dark yellow, microscopic needles. Silver and lead salts are described.

Sodium acetoxychlor- α -naphthaquinonesulphonate,



is obtained by heating 1 part of the disodium salt of the hydroxy-acid with 3 parts of acetic chloride in a sealed tube for eight hours at 100° . It crystallises in bright yellow needles. Both the acid and its salts are characterised by forming double salts, such as $C_{12}H_6SO_7Ag + 2AgNO_3$, and $(C_{12}H_6SO_7)_2Pb + 2Pb(OAc)_2$, both of which crystallise in red needles.

Sodium anilidochlor- α -naphthaquinonesulphonate,



is formed when sodium dichloronaphthaquinonesulphonate (1 mol.) is heated with aniline (2 mols.). The free acid is insoluble in ether, but

readily dissolves in alcohol, and melts at 190° (uncorr.). Both the acid and its salts dye wool and silk a beautiful red, without mordants, and the colour is not changed by acids. The sodium and lead salts are described. With the toluidines and xylydines, the acid forms compounds possessed of dyeing properties.

Dichlor- α -naphthaquinonesulphonic acid has the constitution [$O_2 : Cl_2 : SO_3H = 1 : 4 : 2 : 3 : 3'$]. The β -hydroxyphthalic acid obtained from it melts at 205° (uncorr.), the corresponding anhydride at 167° (uncorr.).
G. T. M.

Characteristics of Partially Hydrogenised Aromatic Substances. By E. BAMBERGER and W. LODTER (*Ber.*, **21**, 836—846).—The bromination of a large number of these compounds has been studied. The same method was employed in all cases; the substance was dissolved in chloroform, cooled to 0° , and a solution of the calculated quantity of bromine in chloroform added drop by drop; after remaining some time in the freezing mixture, the chloroform and excess of bromine were evaporated, and the products purified by recrystallisation, &c.

Dihydronaphthalene dibromide has been already described (*Abstr.*, 1887, 719).

Dihydroacenaphthene dibromide, $C_{12}H_{12}Br_2$, is prepared from tetrahydroacenaphthene (this vol., p. 292) as described above, its formation being accompanied by the elimination of hydrogen as hydrogen bromide. It crystallises in lustrous, thick tables, or in short, highly refractive prisms of the rhombic system; $a : b : c = 0.9996 : 1 : 1.0837$; observed forms, $0P$, $P\infty$, $\bar{P}\infty$, ∞P ; melts at 138° ; and is sparingly soluble in cold, readily in hot alcohol, and in benzene, ether, and chloroform. When heated with alcoholic potash, it yields acenaphthene.

Bromacenaphthene, $C_{12}H_9Br$, is formed simultaneously with the compound last described, which is readily separated from it by crystallisation. It is a pale-yellow, viscid liquid, and boils at $302-307^{\circ}$.

Tetrahydrodiphenyl dibromide, $C_{12}H_{14}Br_2$, is a yellow liquid which cannot be distilled without decomposition, and is sparingly soluble in alcohol, readily in ether and chloroform.

Dihydrodiphenyl, $C_{12}H_{12}$, prepared by treating the preceding compound with alcoholic potash, is an oil, and boils at $247-249^{\circ}$. The *dibromide* is an oil which when heated, either alone or with alcoholic potash, readily loses hydrogen bromide, and is converted into diphenyl.

Bromotetrahydrodiphenyl dibromide, $C_{12}H_{10}Br_3$, is formed by the action of bromine on tetrahydrodiphenyl; it crystallises in strongly refractive, rhombic tables; $a : b : c = 0.6998 : 1 : 0.5376$, observed faces, $\infty P\infty$, $\infty \bar{P}4$, $\bar{P}\infty$, $\infty \bar{P}\infty$, $\infty \bar{P}6$, P ; it melts at 134° , and is sparingly soluble in alcohol and ether, more readily in chloroform and hot benzene.

Bromodihydrodiphenyl, $C_{12}H_{10}Br$, obtained by the action of alcoholic potash on the preceding compound, is a yellow oil which decomposes into diphenyl and hydrogen bromide when heated. The *dibromide* is

a colourless oil which yields a mixture of diphenyl and bromodiphenyl when heated with alcoholic potash.

The authors suggest the following test for partially hydrogenised aromatic compounds. The substance is dissolved in chloroform, and a very dilute solution of bromine in chloroform added, the whole being well cooled; if the colour of the halogen disappears, the solution is evaporated to dryness after treatment with sulphurous acid to remove adhering bromine, dissolved in absolute alcohol, and heated with alcoholic potash, when the separation of potassium bromide renders it probable that the substance belongs to this class. The proof is, however, by no means certain, inasmuch as some other substances give the reaction, whilst anthracene dihydride does not give the test (probably because the additional hydrogen-atoms are attached to the carbon-atoms serving to connect the two benzene-rings). This test was applied to the following substances, the quantities of which were too small for quantitative investigation: tetrahydrophenanthrene, tetrahydrotene, dimethylpiperidine, isonicotine, and cantharic acid, in all cases with positive results.

A. J. G.

Retene from Rosin Oil. By W. KELBE (*Chem. Centr.*, 1837, 1504, from *Ntf.-Vers. zu Wiesbaden*, 60, 242).—Retene can be obtained by heating rosin oil with sulphur until hydrogen sulphide ceases to come off, and then distilling the product.

J. P. L.

Atmospheric Oxidation of Turpentine, Camphor Oil, and Oil of Sunflower. By C. T. KINGZETT (*J. Soc. Chem. Ind.*, 7, 67—69).—The author expresses the opinion that the results which led Yoshida (*Trans.*, 1885, 779) to assert that camphorogenol isolated from camphor oil by fractional distillation constitutes the source from which camphor itself is produced, are not conclusive evidence, since, as all the operations were conducted with free access of air (which was observed by Yoshida to favour the change), it is possible that camphor was produced by the direct oxidation of the terpenes. The author has repeatedly subjected samples of camphor oil to oxidation by air in the presence of water, with the view of ascertaining if the products are identical with those which are furnished by terpenes generally, and found that hydrogen peroxide was freely produced. The formation of the latter necessitates the previous production of camphoric acid, which, unless it be identical in composition with camphorogenol, would complicate the chemistry of the oxidation of camphor oil much beyond Yoshida's expressed views. It would therefore be interesting to know whether camphorogenol yields hydrogen peroxide when brought into contact with water.

The author in experimenting with a specimen of sunflower oil failed to obtain hydrogen peroxide therefrom when oxidised by his process, and concludes that it did not contain any terpene. He was not, however, certain whether this sample was produced from the seeds of the sunflower or from the leaves.

D. B.

Oil of Spike. By R. VOIRY and G. BOUCHARDAT (*Compt. rend.*, 106, 551—553).—The crude product from Ardeche was amber

coloured and had a strong odour; sp. gr. = 0.92, rotatory power, $[\alpha]_D = +1^\circ 24'$. It was fractionated under ordinary pressure below 190° , and under reduced pressure at higher temperatures.

A small fraction boiling at 155 – 160° consisted of a terebenthene with a rotatory power $[\alpha]_D +24^\circ 48'$. It gave a solid hydrochloride melting at 129° with a rotatory power $[\alpha]_D = -1^\circ 54'$. The fraction boiling at 160 – 176° was likewise very small.

The fraction at 176 – 180° , *spikol*, amounted to one-tenth of the weight of the original substance. It has the composition $C_{10}H_{18}O$, solidifies at -25° , and melts at -3° , but after purification by cooling and partial melting, it melts at 0° , and is optically inactive, whilst the mother-liquor has a rotatory power $[\alpha]_D = +7^\circ 0'$. The original fraction at 176 – 178° had a rotatory power $[\alpha]_D = +2^\circ 16'$, and the fraction at 178 – 180° a rotatory power $+1^\circ 20'$; sp. gr. = 0.935; vapour density 5.4.

The purified product seems to be identical with eucalyptol or cajeputol. With hydrogen chloride, it yields a solid hydrochloride, $(C_{10}H_{18}O)_2 \cdot HCl$, which becomes liquid in contact with moist air, or with water, and when treated with water or alkalis yields the original *spikol*. In a vacuum it loses hydrogen chloride on slight rise of temperature. If heated with water in sealed tubes, it yields a dihydrochloride, $C_{10}H_{16} \cdot 2HCl$, together with *spikol*. With bromine, *spikol* yields a cinnabar-red compound, $C_{10}H_{18}OBr_2$, insoluble in light petroleum, and identical with the compound obtained in the same way from *cyneol*.
C. H. B.

Apiole. By G. CIAMICIAN and P. SILBER (*Ber.*, **21**, 913–914).—The authors find that *apiole* boils at 179° at 34 mm., and at 294° at the ordinary pressure, and that its composition is $C_{12}H_{14}O_4$ (compare v. Gerichten, this Journal, 1876, ii, 533). It is volatile with steam, and dissolves in the ordinary organic solvents, but combines neither with acids nor with bases, and does not react with hydroxylamine and phenylhydrazine. When oxidised, either in aqueous or acetic acid solution, with chromic acid mixture, it is converted into a compound, $C_{10}H_{10}O_5$, which crystallises from dilute alcohol in needles, melts at 102° , and is sparingly soluble in water and light petroleum, readily soluble in alcohol, ether, benzene, carbon bisulphide, and acetic acid. Concentrated sulphuric acid dissolves it with an intense yellow colour, which changes to olive-green on warming. A small quantity of a volatile acid is also formed during the oxidation, but the quantity obtained was insufficient to admit of its nature being determined. When *apiole* is oxidised with potassium permanganate, an acid and a neutral compound melting at 122° are formed. Further results are promised.
W. P. W.

Strophanthin. By T. R. FRASER (*Proc. Roy. Soc. Edin.*, **124**, 370–374).—In former communications, the author described a compound to which the name *strophanthin* has been given, and which is obtained from the seeds of *Strophanthus hispidus*. Various seeds which have been examined since those communications do not all yield identical substances, therefore a fresh examination has been under-

taken. The former and impure products obtained by means of alcohol and ether were dissolved in water, tannin was added, and the tannate precipitated with freshly precipitated lead oxide, and extracted with rectified spirit. This extract was then mixed with ether, and the precipitate finally dissolved in dilute alcohol, and the lead precipitated by carbonic anhydride. Filtration and drying in a vacuum yielded a translucent, gummy mass, which afterwards became white and opaque. This strophanthin is faintly acid, of an intense, bitter taste, freely soluble in water, less so in spirit, insoluble in ether and chloroform, and does not contain nitrogen. Its composition appears to be $C_{26}H_{14}O_{14}$. All the mineral and some of the organic acids decompose strophanthin into glucose and *strophanthidin*, which crystallises readily from a 1.5 per cent. solution of sulphuric acid, but a further decomposition, accompanied with formation of glucose, appears to be produced when the solution of strophanthin in 1.5 per cent. sulphuric acid is boiled for four hours; 4.3 per cent. of a brown, amorphous compound being formed. From this it would seem that an acid is not the best substance to produce strophanthidin from strophanthin, and it is probable that Hardy and Gallois' strophanthin was strophanthidin. A long account of reactions is also given.

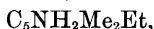
E. W. P.

Unorganised Ferments. By O. LÖEW (*J. pr. Chem.* [2], **37**, 101—104).—The author, whilst admitting that in the preparation of diastase by precipitation with lead acetate a product is obtained which is slightly impure owing to the presence of dextrin-like substances, denies that the diastase loses its activity (see Abstr., 1887, 165). If the compound analysed by Lintner is not a mixture, a difference must exist between animal and vegetable diastase, the former being an albuminoid, the latter an albuminoid combined with some other substance.

When 0.1 gram of diastase, possessing great activity, but still containing dextrin-like substances, was placed in a dilute solution containing 0.15 gram of hydroxylamine, it was rendered completely inactive at the end of 24 hours. Diastase is also readily rendered inactive by relatively small quantities of nitrous acid at 40°. Pepsin and diastase both lose their activity when allowed to remain in contact with a dilute solution of formaldehyde (1 gram of ferment, 10 grams water, and 5 c.c. of a 15 per cent. solution of formaldehyde) for one day. Some ferments, emulsin, papayotin, trypsin, and other albuminoids give with formaldehyde precipitates soluble with difficulty in alkalis and acids. Perhaps the loss of activity which the unorganised ferments suffer in presence of acids and alkalis by warming to 80° and under other influences, is due to isomeric change in the amido- and aldehyde-groups contained in the ferments.

G. T. M.

New Parvoline (Dimethylethylpyridine). By E. DÜRKOPF and M. SCHLAUGK (*Ber.*, **21**, 832—836).—*Dimethylethylpyridine*,



is prepared by heating propaldehydeammonia (1 mol.) and paralde-

hyde ($= 3 \text{ mol. C}_2\text{H}_4\text{O}$) in sealed tubes for 10 hours at 210° . The reddish-brown, oily mass obtained is distilled with steam, the aqueous distillate strongly acidified with hydrochloric acid, evaporated, the hydrochlorides decomposed with potash and fractionally distilled. The fraction $180\text{--}200^\circ$ of the bases is then converted into the mercuriochlorides; by this means, as the new parvoline mercuriochloride is nearly insoluble in cold water, a separation from collidine and other bases of lower boiling point is readily effected. It is a clear, colourless, strongly refractive, mobile liquid of mild, agreeable, sweetish odour, boils at 188° , has sp. gr. 0.94185 at 0° , 0.92894 at 16° (water at $4^\circ = 1$). It is less soluble in hot than in cold water. The *mercuriochloride*, $\text{C}_5\text{NH}_{13}\cdot\text{HCl}\cdot 3\text{HgCl}_2$, forms long, lustrous, pure white, spear-shaped needles, or small, well-formed tables of rhombic habit, and melts at 116° . The *platinochloride*, $(\text{C}_5\text{NH}_{13})_2\cdot\text{H}_2\text{PtCl}_6$, crystallises in large, tabular, triclinic forms. The *aurochloride* forms lustrous, citron-yellow needles or thin plates, and melts at $86\text{--}87^\circ$. The *picrate* melts at 152° .

Methylpyridinedicarboxylic acid, $\text{C}_5\text{NH}_2\text{Me}(\text{COOH})_2$, prepared by the oxidation of the parvoline with a 2 per cent. solution of potassium permanganate, crystallises in small, thin, rhombic plates, melts at 225° , and is sparingly soluble in hot water. By the further oxidation of the parvoline, a *pyridinetricarboxylic acid*, $\text{C}_5\text{NH}_2(\text{COOH})_3$, was obtained, which forms hard, globular, crystal aggregates, melts at 318.7° (corr.) with intumescence, and is readily soluble in hot water. It gives a blood-red coloration with ferrous sulphate, a yellow coloration with ferric sulphate, a blue, crystalline precipitate with copper sulphate. Although all six possible pyridinetricarboxylic acids are known, it has not yet been possible to identify this acid with certainty with any one of them. It closely resembles Weber's carbodinicotinic acid (Abstr., 1887, 1118) in its whole behaviour, but that is described as melting at 223° and crystallising with $1\frac{1}{2}$ mol. H_2O .

A. J. G.

α -Stilbazole (α -Cinnamylpyridine) and its Reduction Products. By H. BAURATH (*Ber.*, 21, 818—825; compare this vol. p. 65).—The author has changed the name of this substance from α -cinnamylpyridine to α -stilbazole. It boils at $324\text{--}325^\circ$ (corr.) under 750 mm. pressure; its alcoholic solution is without action on litmus. The *hydrochloride*, $\text{C}_{13}\text{H}_{11}\text{N}\cdot\text{HCl} + 4\text{H}_2\text{O}$, crystallises in concentrically grouped needles, and when anhydrous melts at 177° . The *platinochloride*, $(\text{C}_{13}\text{H}_{11}\text{N})_2\cdot\text{H}_2\text{PtCl}_6 + 2\text{H}_2\text{O}$, forms small, reddish-yellow needles which begin to melt with slight evolution of gas at 181° , and are completely fused at 188° without carbonisation. The *aurochloride*, $\text{C}_{13}\text{H}_{11}\text{N}\cdot\text{HAuCl}_4$, forms sparingly soluble, cinnabar-red crystals, and melts at 185° . The *mercuriochloride*, $\text{C}_{13}\text{H}_{11}\text{N}\cdot\text{HHgCl}_3 + \text{H}_2\text{O}$, melts at $181\text{--}183^\circ$. The *periodide*, $\text{C}_{13}\text{H}_{11}\text{N}\cdot\text{HI}\cdot\text{I}_2$, crystallises in prisms of bluish lustre, which in very thin layers transmit reddish-violet light. When oxidised, stilbazole yields benzoic and picolinic acids.

Dihydro- α -stilbazole, $\text{C}_5\text{NH}_4\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$ [$\text{CH}_2 = 2$], is prepared by heating stilbazole with five times the quantity of fuming hydriodic acid for one hour, the new compound separating as its periodide. It

is liquid at ordinary temperatures, but can be solidified by long exposure to a low temperature, and then melts at -3° ; it boils at 289.5° (corr.) under 766 mm. pressure, has a sweet, agreeable odour, is sparingly soluble in water, miscible in all proportions with alcohol, ether, and benzene, and volatilises with steam. Sp. gr. at $0^{\circ} = 1.0465$ (water at $4^{\circ} = 1$). The *hydrochloride* and *sulphate* crystallise in small needles; the *platinochloride*, $(C_{13}H_{13}N)_2 \cdot H_2PtCl_6$, forms small, reddish-yellow needles, and melts at $185-186^{\circ}$; the *aurochloride*,



is the most characteristic salt; it forms lustrous, yellow needles several cm. long, sinters at 145° , and melts at $149-150^{\circ}$; the *mercuerochloride*, $C_{13}H_{13}N, H_2HgCl_4$, is sparingly soluble, and melts at 149° .

α -Stilbazoline, $C_6NH_{10} \cdot CH_2 \cdot CH_2Ph$, is prepared by adding sodium to a hot solution of α -stilbazole in absolute alcohol, decomposing the product with water, acidifying, distilling off the alcohol, and concentrating the aqueous solution on the water-bath; a considerable amount of liquid hydrocarbons formed as bye-products in the reaction have to be removed by aid of a separating funnel. The concentrated solution is then slightly acidified and treated with sodium nitrite in the warm for some time, when the nitroso-derivative of stilbazoline separates in large, reddish drops; this is extracted with ether and the ether distilled off. As the nitrosamine cannot be distilled, it is decomposed with hydrogen chloride, the reaction, at first very violent, being moderated by cooling, but later on assisted by heating. The product is largely diluted, extracted several times with ether to remove any unaltered nitrosamine, and the base finally liberated by treatment with alkali. It is a slightly oily liquid, does not solidify in a mixture of carbonic anhydride and ether, boils at 288° (corr.) under 760 mm. pressure, has sp. gr. 0.9874 at 0° (water at $4^{\circ} = 1$), and is sparingly soluble in water, miscible in all proportions with alcohol, ether, and benzene. Litmus-paper is not affected by the dry base, but in presence of water is turned blue. The *hydrochloride*, $C_{13}H_{13}N, HCl$, forms slender, colourless needles, and melts at 155° ; the *platinochloride*, $(C_{13}H_{13}N)_2 \cdot H_2PtCl_6$, melts at $187-189^{\circ}$, and begins to decompose at 190° ; the *aurochloride* melts at $133-134^{\circ}$; the *mercuerochloride* and *periodide* were only obtained as oils. Stilbazoline resembles conine in its physiological action, but is less active, the lethal doses per 1 kilo. body-weight being 0.07578 for conine and 0.09614 for α -stilbazoline.

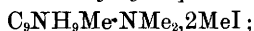
The difference in the atomic volumes of dihydro- α -stilbazole and α -stilbazoline corresponds with a value of 5.5 for H_2 , a number agreeing approximately with that obtained by Horstmann (Abstr., 1887, 546) in the pyridine series. A. J. G.

Molecular Migrations in the Quinoline Series. By J. ZIEGLER (Ber., 21, 862-867).—*Paramidotetrahydroquinoline*, $C_9NH_{10} \cdot NH_2$, is prepared by reducing Fischer and Hepp's tetrahydronitrosoquinoline (Abstr., 1887, 729) with tin and hydrochloric acid; it forms strongly refractive, transparent, rhombic crystals, melts at 97° , can be distilled unchanged under reduced pressure, and is soluble in ether and benzene. The aqueous solution gives a violet coloration with ferric chlo-

ride, which on addition of hydrochloric acid changes to emerald-green. The same substance is obtained by reduction of La Coste's paramidoquinoline with tin and hydrochloric acid. The *hydrochloride*, $C_9H_{12}N_2 \cdot 2HCl$, forms snow-white, hygroscopic needles, and melts at $244-246^\circ$; the *platinochloride*, $C_9H_{12}N_2 \cdot H_2PtCl_6$, is a yellow, crystalline powder; the *picrate* forms satiny, siskin-green crystals melting at 176° ; the *oxalate* melts at 168° . The *diacetyl*-compound, $C_9H_{12}N_2 \cdot Ac_2$, crystallises in concentrically-grouped white needles, and melts at 172° .

In addition to the method given by La Coste (Abstr., 1883, 811), paramidoquinoline can be prepared by converting sulphanilic acid into paraquinolinesulphonic acid by Skraup's method, converting this into parahydroxyquinoline by fusion with potash, and heating the latter with ammonio-zinc chloride for 10 hours at $270-280^\circ$.

When paramidoquinoline is dissolved in methyl alcohol and heated with excess of methyl iodide in a reflux apparatus for some hours, it is converted into *dimethamidomethylhydroquinoline dimethiodide*,



this forms nearly white crystals melting at 171° .

Paradinitrosotetrahydroquinoline, $C_9H_9N_2O_2$, is prepared by treating an acetic acid solution of paranitrosohydroquinoline with the calculated quantity of sodium nitrite; it forms long, moss-green needles, melts at 98° , and explodes at a slightly higher temperature; it gives Liebermann's reaction.

When solutions of paranitrosohydroquinoline and phenylhydrazine are mixed, a substance crystallising in lustrous, yellow plates is obtained; it melts at 126° with explosion.

When toluquinoline is converted from orthotoluidine is hydrogenised and converted into the corresponding nitroso-compound, a heavy, yellowish oil is obtained. When this is dissolved in an equal quantity of absolute alcohol and as much again alcoholic hydrogen chloride added, there separates after some hours the hydrochloride of the isomeric nitroso-compound. By treatment with ammonia, the free base $C_{10}H_{12}N_2O$ is obtained, and after crystallisation from benzene forms steel-blue crystals of metallic lustre which melt at 140° . When reduced, it yields a paramidotoluhydroquinoline, whose aqueous solution gives with ferric chloride the characteristic red coloration, turning emerald-green on addition of hydrochloric acid; the *hydrochloride*, $C_{10}H_{16}N_2Cl_2$, melts at 166° .

Paranitrosotetrahydroquinoline is converted into paramidoquinoline under certain conditions; this change occurs very slowly if the substance is moistened with hydrochloric acid and left to itself, or if the hydrochloride is heated at 105° , but it is most complete if an aqueous solution of the hydrochloride is left for some days in the warm or is heated in a reflux apparatus for a few hours. A. J. G.

Orthohydroxyquinaldinecarboxylic Acid. By W. KÖNIG (Ber., 21, 883—884).—*Orthohydroxyquinaldinecarboxylic acid*,



is prepared by heating the potassium compound of orthohydroxquin-

aldine with liquid carbonic anhydride in an autoclave for six to seven hours at 180—190°. It crystallises with 1 mol. H_2O in long, golden-yellow needles, becomes anhydrous at 120°, and melts at 207° with decomposition into orthohydroxyquinaidine and carbonic anhydride. It is sparingly soluble in cold, more soluble in hot water or alcohol, insoluble in ether. The aqueous solution gives a cherry-red coloration with ferric chloride.

A. J. G.

Sparteine. By F. B. AHRENS (*Ber.*, **21**, 825—832).—As the reduction and oxidation of sparteine (Abstr., 1887, 1056) threw no light on its constitution, it seemed necessary to have recourse to more energetic reactions in order to investigate this question.

When sparteine is heated with seven to eight times its weight of 57 per cent. hydriodic acid for five hours in sealed tubes at 200°, it yields methyl iodide and a new base, $C_{14}H_{24}N_2$, which distils at about 276°, and has a strong, peculiar odour. Its platinochloride forms small, yellowish-red crystals, and blackens and decomposes at 230°; the aurochloride melts at 157°. As it readily yields a nitroso-compound, it must be a secondary base, and it follows that the eliminated methyl-group must have been united to nitrogen.

When sparteine is distilled with five times its weight of lime, it yields ethylene, propylene, γ -picoline, and a very small quantity of a tertiary base that could not be identified with certainty, whilst when passed through tubes heated to dull redness, pyridine, γ -picoline, a small quantity of a secondary base, ethylene, propylene, non-aromatic hydrocarbons, ammonia, and hydrogen cyanide are obtained. The aurochloride of the secondary base melts at 172°.

From these investigations the author considers it probable that the sparteine molecule contains two pyridine-rings, and that these are hydrogenised, seeing that pyridinecarboxylic acids cannot be obtained on oxidation (*loc. cit.*), nor can more than two hydrogen-atoms be taken up. With regard to the side-chains, there is one methyl-group attached to nitrogen and another united to one pyridine-ring at the γ -position, and probably also there is a side-chain of three carbon-atoms.

A. J. G.

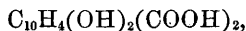
Optical Rotatory Power of Papaverine. By G. GOLDSCHMIEDT (*Monatsh.*, **9**, 42—44).—Several observations made with pure papaverine show that the compound is inactive. The results confirm the correctness of the Bel-Van't Hoff theory, and at the same time give important support to the author's papaverine formula (Abstr., 1886, 478). As papaverine and laudanine were hitherto the only exceptions to the rule that derivatives of active substances are also active, and as papaverine is shown in the present paper to form no exception, it is suggested that a renewed examination of laudanine is desirable (compare Hesse, *Annalen*, **176**, 198).

N. H. M.

Narceine. By A. CLAUS and A. MEIXNER (*J. pr. Chem.* [2], **37**, 1—9).—In a previous paper (Abstr., 1885, 996), one of the authors describes a substance obtained by treating commercial narceine with

potassium permanganate. This proves to be pure narceine; it melts at 162° (uncorr.). The platinumchloride $(C_{23}H_{23}NO_9)_2 \cdot H_2PtCl_6$, crystallises in golden-yellow needles, melting at 195° (uncorr.).

On oxidising narceine (1 mol.) with potassium permanganate ($4\frac{1}{2}$ mols.), *narceinic acid*, $C_{15}H_{15}NO_8 + 3H_2O$, is formed. It crystallises from hot water in forms belonging to the rhombic or monoclinic system. The trisodium salt, $C_{15}H_{12}NO_8Na_3$, dissolves readily in water, from which it is precipitated by alcohol. The disodium salt, $C_{15}H_{13}NO_8Na_2 + 5H_2O$, crystallises from water in small, colourless needles, melting at 85° (uncorr.). The monosodium salt, $C_{15}H_{14}NO_8Na + 4\frac{1}{2}H_2O$, also crystallises in small needles, and dissolves readily in water. The barium salt, $(C_{15}H_{12}NO_8)_2Ba_3 + 5H_2O$, is fairly soluble in water. At $180-200^{\circ}$, narceinic acid yields carbonic anhydride, dimethylamine, and a *dihydroxynaphthalenedicarboxylic acid*,



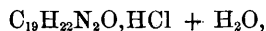
which is best purified by sublimation, and crystallises in long needles, melting at 162° (uncorr.). It dissolves readily in ether and chloroform, but is almost insoluble in water and alcohol. Both the normal sodium salt, $C_{12}H_6O_6Na_2 + 6OH_2$, and the acid salt, $C_{12}H_7O_6Na + 5\frac{1}{2}H_2O$, crystallise in small, colourless needles. On reduction with hydriodic acid, a naphthalenedicarboxylic acid is formed, melting at $250-253^{\circ}$, and seeming to agree in properties with the γ -naphthalenedicarboxylic acid described by Wichelhaus and Darmstädter (*Annalen*, **152**, 309).

G. T. M.

Cinchonigine. By E. JUNGFLEISCH and E. LÉGER (*Compt. rend.*, **106**, 357—360).—*Cinchonigine*, $C_{19}H_{22}N_2O$, is obtained by heating the hydrochloride (this vol., p. 380 and 507) with soda and extracting with ether. When the ether is distilled off, an oily residue is left, which in contact with dry air gradually changes to a colourless, crystalline mass. If recrystallised from anhydrous ether, cinchonigine forms short, bulky, highly refractive, colourless prisms, which melt at 128° . It distils regularly under reduced pressure. In a 1 per cent. solution in alcohol of 97° , the rotatory power $[\alpha]_D = -60.1^{\circ}$; in a solution of half the strength, $[\alpha]_D = -61.16^{\circ}$. In a 1 per cent. solution in hydrochloric acid containing 2 mols. of the acid to each molecule of base, $[\alpha]_D = -40.70^{\circ}$; with twice the proportion of acid $[\alpha]_D = -38.21^{\circ}$.

Cinchonigine is slightly soluble in water, and is alkaline to litmus, but neutral to phenolphthalein. It is very soluble in methyl, ethyl, and amyl alcohols, chloroform, benzene, and acetone, but is less soluble in anhydrous ether. The acid solutions are not fluorescent. Cinchonigine yields the same products of decomposition as cinchonine.

Cinchonigine forms basic salts which are feebly alkaline to litmus, and normal salts which have an acid reaction and are usually crystalline, stable, and soluble in water. The *basic hydrochloride*,



forms large, colourless, highly refractive, prismatic needles, which

melt at 213° , and decompose without volatilising. It is only slightly soluble in cold water but dissolves more readily at 100° . In a 1 per cent. aqueous solution, the rotatory power $[\alpha]_D = -65.41^{\circ}$. The *platinochloride*, $C_{19}H_{22}N_2O, H_2PtCl_6 + H_2O$, forms small, bright-orange prisms only slightly soluble in warm water. The *basic hydrobromide*, analogous in composition to the chloride, crystallises from boiling water in short, slightly efflorescent prisms, which melt at 218.5° , and are only slightly soluble in cold water. The *basic hydriodide* crystallises in non-efflorescent, prismatic needles, which melt at 223° . The *normal hydriodide*, $C_{19}H_{22}N_2O, 2HI + H_2O$, is obtained by cooling a solution of the preceding compound mixed with hydriodic acid. It forms bright-yellow crystals, which are only slightly soluble in water, and are decomposed by light, with liberation of iodine. The *normal dextrotartrate* crystallises with 7 mols. H_2O in long, prismatic needles. It is much less soluble than the basic tartrate. The *basic oxalate* forms needles, which if left in the mother-liquor change to large, efflorescent, very soluble tables, containing 5 mols. H_2O . The same crystals are obtained by spontaneous evaporation of the solution. The *basic chromate* is crystalline; the *basic sulphate* forms highly soluble needles; the *thiocyanate* is crystalline and only slightly soluble, and unites with zinc thiocyanate to form a bulky, amorphous, colourless, insoluble compound; the *aurochloride* is pale-yellow and amorphous.

Cinchonigine methiodide, $C_{19}H_{22}N_2O, MeI$, obtained by mixing ethereal solutions of cinchonigine and methyl iodide, crystallises from alcohol in colourless, anhydrous needles, which melt with decomposition at 253° . It is slightly soluble in water or cold alcohol, very soluble in chloroform, acetone, and amyl alcohol; insoluble in ether or benzene. Methyl chloride forms an analogous compound.

Cinchonigine ethiodide, obtained in a similar manner, forms large, lemon-yellow prisms, which contain $2H_2O$. It melts at 232° , with slight decomposition, and is more soluble than the methyl-derivative in alcohol or water. Ethyl bromide forms a similar compound, which melts at 217° with decomposition, and is very soluble in water, chloroform, ethyl alcohol, and acetone, but is insoluble in ether or benzene.

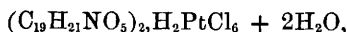
C. H. B.

Colchicine. By S. ZEISEL (*Monatsh.*, 9, 1—30; compare Abstr., 1887, 284).—Determinations of methoxyl (Abstr., 1886, 493 and 1079), in colchicine and colchiceïne, showed that the former contains four, and the latter three methoxyl-groups.

When colchiceïne is heated on a water-bath with hydrochloric acid, acetic acid distils, and a mixture of the hydrochlorides of trimethyl-colchicine, dimethylcolchiceinic and colchicinic acids are obtained. The residue is diluted with a little water, and extracted with chloroform, which takes up only the first mentioned of the three hydrochlorides.

Trimethylcolchiceinic acid, $COOH \cdot C_{15}H_9(OMe)_3 \cdot NH_2$, is obtained by precipitating the hot aqueous solution of the hydrochloride with the exact amount of potash; it forms microscopic prisms, with 2 mols. H_2O , melts at 159° , and decomposes when heated for a long time at 150° . The *hydrochloride* forms lustrous, yellowish-white plates, moderately soluble in cold water, with bright-yellow colour; the aqueous solution

reddens litmus. In its general behaviour to alkaloid reagents, it resembles colchiceïne hydrochloride. The *platinochloride*,



crystallises in groups of yellow needles.

Dimethylcolchicinic acid, $COOH \cdot C_{15}H_9(OMe)_2(OH) \cdot NH_2$, is prepared by precipitating a 2 per cent. solution of the hydrochloride with the necessary amount of aqueous soda; the crystals (with $4\frac{1}{2}$ mols. H_2O) melt at $141-142^\circ$. The *hydrochloride* (with 1 mol. H_2O) is rather sparingly soluble in water and alcohol.

Colchicinic acid, $COOH \cdot C_{15}H_9(OH)_3 \cdot NH_2$, was not obtained quite pure, or in a crystalline form. The dilute hydrochloric acid solution gives an intense brownish-red coloration with ferric chloride.

Acetotrimethylcolchicinamide, $NHAc \cdot C_{15}H_9(OMe)_3 \cdot CONH_2$, is formed when 10.5 grams of colchicine is heated with 15 c.c. of 5 per cent. alcoholic ammonia for four hours at 100° . A reaction seems to take place in the cold, as the mixture becomes red after some hours, or greenish when seen in thin layers. The liquid shows a characteristic absorption spectrum; this disappears after the solution has been heated for four hours at 100° . The amide is crystallised from hot alcohol, from which it separates in two forms, of which the one crystallises in the rhombic system, with 1 mol. $EtOH$. It is readily soluble in dilute hydrochloric acid; almost insoluble in water. When the alcoholic solution is heated with aqueous soda at 110° , colchiceïne is formed. The *hydrochloride*, *platinochloride*, and *aurochloride* were prepared. The solution of the base in dilute alcohol gives an intense brown coloration with ferric chloride. When the strong hydrochloric acid solution of the amide is treated with a small amount of potassium nitrite, it acquires a splendid violet colour. Several other reactions are described.

N. H. M.

Compounds of Gelatin with Tannin. By C. BÖTTINGER (*Annalen*, **244**, 227—232).—The precipitate produced by gelatin in a solution of tannin contains 16.5 per cent. of nitrogen, corresponding with 34 per cent. of tannin. The precipitate is decomposed by water at 150° , yielding a solution which gives an abundant precipitate with tannin.

The precipitate produced by gelatin in a solution of oak-bark tannin contains 9.5 per cent. of nitrogen, corresponding with 42.7 per cent. of tannin. It is decomposed by water at 150° , yielding three products, which are respectively freely soluble in cold water, soluble in hot, and insoluble in water.

Hide tanned with oak-bark behaves in a similar way. The portion insoluble in water slowly dissolves in alkalis and alkaline carbonates.

W. C. W.

Urohæmatoporphyrin and Allied Pigments. By C. A. MACMUNN (*Proc. Physiol. Soc.*, 1888, 5—6).—In the study of urinary pigments, it is necessary to pay attention to certain feeble bands in the red half of the spectrum which have been overlooked by many previous observers. The following reagents, ammonia, ammonio-zinc chloride, zinc chloride alone, and aqueous soda, cause cha-

racteristic changes in urinary pigments. From a study of these changes, the following conclusions are drawn:—(1.) Two entirely distinct substances have been included by physiologists under the name urobilin, namely, that of normal and that of pathological urine. (2.) Hydrobilirubin is not identical with either. (3.) Normal urobilin is identical with a pigment produced by the action of peroxide of hydrogen on acid hæmatin, and subsequent brief reduction with sodium amalgam; pathological urobilin cannot as yet be traced definitely to its source, but it is very closely related to normal urobilin. (4.) Hydrobilirubin and human stercobilin are not identical; but in the cat the pigment of the fæces appears to be hydrobilirubin. (5.) Stercobilin and pathological urobilin appear to be closely connected; both are probably derived from hæmatin, and not directly from biliary pigments. (6.) Urohæmatoporphyrin (called by le Nobel isohæmatoporphyrin, see Abstr., 1887, 1127) is beyond doubt a reduction product of hæmatin, and the urobilinoidin of le Nobel is its chromogen; this chromogen is sometimes present in pathological urine. Urohæmatoporphyrin has been found in the urine of patients suffering from rheumatism, pericarditis, Addison's disease, cirrhosis of the liver, croupous pneumonia, Hodgkin's disease, measles, typhoid fever, and meningitis. The band at F in the spectrum of this substance is not removed by ammonia; in this it resembles stercobilin, but differs from urobilin and from hydrobilirubin.

W. D. H.

Physiological Chemistry.

Influence of Diet on the Elimination and Absorption of Carbon. By M. HANRIOT and C. RICHET (*Compt. rend.*, **106**, 419—422).—An account of experiments on the products of respiration of a man existing on a mixed diet of nitrogenous, fatty, and amylaceous food. The influence of each ingredient in the diet will be determined by subsequent experiments. The ratio of oxygen absorbed to carbonic anhydride produced remains constant under constant conditions, hence it would seem that respiration is regulated automatically. During digestion the ratio rises, that is to say there is an increased absorption of oxygen. C. H. B.

Influence of Diet on Respiratory Changes. By M. HANRIOT and C. RICHET (*Compt. rend.*, **106**, 496—498).—This paper contains details of experiments which show that respiration is increased by taking food, but almost solely when the food consists of carbohydrates. Nitrogenous and fatty foods have little effect on the respiratory process. Amylaceous food increases the volume of air respired and the quantity of oxygen absorbed, but its effect is most strongly marked in the increased production of carbonic anhydride. The percentage proportion of oxygen absorbed and carbonic anhydride produced varies but little during repose. The

oxygen absorbed amounts on an average to 4.2 per cent. of the air inspired, with variations between 3.4 and 4.7, whilst the quantity of carbonic anhydride produced is on an average 3.4 per cent. of the air expired, with variations between 2.7 and 4.2. A healthy adult man inspires 8 litres of air per hour per kilogram of body-weight, with formation of 0.5 gram of carbonic anhydride and absorption of 0.45 gram of oxygen. During digestion, the volume of air inspired increases to 9 litres per kilogram per hour, with formation of 0.6 gram of carbonic anhydride and absorption of 0.5 gram of oxygen.

C. H. B.

Volatile Bases in the Blood and Breath. By R. WURTZ (*Compt. rend.*, **106**, 213—214).—The air expired from the lungs was passed into a 1 per cent. solution of oxalic acid, care being taken to prevent the introduction of saliva or solid particles. When several cubic metres had been passed through, the liquid was neutralised with calcium carbonate, mixed with a few drops of lime-water, filtered, exactly neutralised with hydrochloric acid, and evaporated in a vacuum. Ammonium chloride is the chief product, but is mixed with the hydrochloride of an organic base which gives precipitates with Boucharlat's reagent and mercuric potassium iodide. It forms a soluble aurochloride, and a soluble platinochloride which crystallises in short needles and seems to be identical with the platinochloride of a volatile base obtained from the blood. A solution of the hydrochloride heated at 100° has a peculiar and characteristic odour.

C. H. B.

Action of Acids on the Functional Activity of the Human Stomach and their Therapeutical Application. By W. JAWORSKI (*Chem. Centr.*, 1887, 1560—1561, from *D. Med. W.*, **13**, 792—796).—The results of the investigation of the action of hydrochloric, lactic, acetic and carbonic acids are as follows:—(1.) The mucus is precipitated in the stomach by the acids. (2.) Cell nuclei appear in the stomach contents, especially after the introduction of hydrochloric acid. (3.) The stomach contents show an increased biuret reaction, again most marked after hydrochloric acid. (4.) Large doses of acid usually cause an inflow of bile into the stomach. (5.) The secretion of pepsin is assisted materially by acids, whilst the secretion of hydrochloric acid is only very slightly influenced, or not more so than it would be by the introduction of distilled water. (6.) 200 c.c. of normal acid disappear from the stomach in $1\frac{1}{4}$ to $1\frac{1}{2}$ hours. (7.) After long-continued consumption of acid, the secretion of hydrochloric acid was checked. (8.) With large quantities of hydrochloric acid, the subjective stomach symptoms do not appear, or only in a slight degree. (9.) The difference between the action of acids and salts of the alkalis on the digestive function of the stomach is that alkalis dissolve mucus and hinder secretion of pepsin, whereas acids precipitate the mucus and induce the secretion of pepsin. After the disappearance of alkalis from the stomach, an increased secretion of hydrochloric acid follows, but after the disappearance of acids there is none, or only a slight secretion.

Both agree in this, that after long use in large quantities they check the secretion of hydrochloric acid or cause it to cease.

In mucous catarrh of the stomach which accompanies in most cases carcinoma of the stomach, the acidity and the secretion of pepsin are probably reduced by the action of the mucus. In pathological cases of this kind, a larger quantity of hydrochloric acid should be used for therapeutical purposes. The author supplements his previous statements respecting carbonic anhydride. Carbonic anhydride both as a gas and dissolved in water favours the secretion of hydrochloric acid (in contradistinction to the above-mentioned acids) and pepsin and consequently the digestive power of the gastric juice. It assists also in increasing the mechanical activity of the stomach.

The concluding part of the paper contains remarks on the clinical use of the acids. J. P. L.

Amount of Acid in the Stomach on an Amylaceous Diet. By J. ROSENHEIM (*Chem. Centr.*, 1887, 1561, from *Med. Centr.*, 25, 865—866).—In healthy subjects, after ingestion of 50 grams of wheaten bread and 150 c.c. of water, the following results were obtained:—(1.) 15 minutes after the commencement of the experiment 0·3 part in 1000 of free hydrochloric acid was present, the quantity quickly increased to 1 part in 1000 after 30 minutes; at which point it remained constant until the complete elimination of the chyme from the stomach. (2.) Lactic acid is present throughout in moderately uniform amount. (3.) Volatile acids are always present although only in traces. In pathological conditions, the free hydrochloric acid present 15 minutes after the commencement of the experiment varies from 0·1 in 1000 in carcinoma to 1 in 1000 in abnormal acidity. After ingestion of pure carbohydrates on an empty stomach, the free hydrochloric acid both in normal and pathological cases was sensibly less than in the previous experiment. Only 0·2 part of hydrochloric and 0·2 part of lactic acid in 1000 were found after one hour's digestion.

Finally, if boiled starch is introduced into the stomach with careful exclusion of saliva, large quantities of hydrochloric acid and an approximately equal amount of lactic acid were always found.

J. P. L.

Free Hydrochloric Acid in the Stomach Contents. By A. GUNZBURG (*Chem. Centr.*, 1887, 1560, from *Med. Centr.*, 40).—The method depends on the phloroglucinol-vanillin test of Wiesner and Singer, which gives a red colour with hydrochloric acid. The reagent consists of 2 parts of phloroglucinol, 1 part of vanillin, and 30 parts of rectified spirit. A few drops of the filtered gastric juice is mixed with a like quantity of the reagent and carefully evaporated in a small capsule, red crystals or, if much organic matter (especially peptone) be present, a red paste is formed. The reaction takes place with 1 part hydrochloric acid in 10,000, but not with 1 in 20,000.

In many cases in consequence of acid albuminates, there is no reaction. For quantitative estimations, the reaction is not of much value, although an approximation can be obtained by diluting the original gastric juice gradually with successive known quantities of water until the limit of reaction 1 in 20,000 is attained. J. P. L.

Does Cellulose Economise the Decomposition of Proteid in the Nutrition of Herbivora? By H. WEISKE (*Zeit. Biol.*, **24**, 553—561).—v. Knierem (this vol., p. 515) has recently again disputed the conclusions arrived at by Weiske and others on this subject. The present paper is a reply to his recent criticisms, and in it the author again affirms that cellulose does not economise the decomposition of proteid, and also points out that v. Knierem's own experiments may be so interpreted as to support this statement.

W. D. H.

Changes Effected by Digestion on Fibrinogen and Fibrin. L. C. WOOLDRIDGE (*Proc. Roy. Soc.*, **43**, 367—368).—Fibrinogen is a name conveniently given to a group of proteids which can be converted into fibrin, which exist in blood plasma, and can be obtained from almost all animal tissues. They are all extremely easily changed by precipitation, are soluble in water (as casein is dissolved in milk), and are readily precipitated by acetic acid and dilute mineral acids in excess, but soluble in greater excess. On adding pepsin to the acid solutions, a precipitate appears in the course of a few hours, which is soluble in dilute alkalis, and on incineration leaves an acid ash which is rich in phosphorus. The phosphorus is stated to be present in the form of lecithin. The ash also contains iron. The fibrin which is formed from these fibrinogens is stated also to contain lecithin, but is entirely soluble in artificial gastric juice. Ordinary fibrin obtained by whipping blood always leaves an undigested residue, due partly to the presence of admixed white corpuscles (Hammarsten), partly, however, to its containing unchanged fibrinogen.

W. D. H.

Influence of Bile on Digestion. By S. H. C. MARTIN and D. WILLIAMS (*Proc. Physiol. Soc.*, 1888, 1).—In artificial digestion experiments, it was found that bile acids very considerably accelerated the amylolytic action of the pancreatic juice. Varying percentages of pig's bile in a solution of starch (2 per cent.) were used, and glycerol extract of pig's pancreas added. A control experiment was always made with bile and starch alone. It was found that the iodine reaction of starch disappeared more rapidly from the solution containing bile and pancreatic extract than from that containing pancreatic extract alone, and that the rapidity of disappearance was proportionate to the amount of bile present up to 4 per cent., beyond which experiments were not performed.

W. D. H.

Influence of Bile on the Digestion of Fats. By A. DASTRE (*Compt. rend.*, **106**, 217—220).—It is known that in the rabbit the pancreatic juice alone is not sufficient to effect the digestion of fats. The author's experiments on dogs by means of a cholecysto-intestinal fistula, produced artificially, show that bile alone is equally unable to effect this change. It follows that the simultaneous action of the pancreatic juice and the bile is essential, and it would seem that bile promotes absorption of the fats, whilst the pancreatic juice is an active agent in their decomposition.

C. H. B.

Stability of Carbonic Oxide and Oxalic Acid in the Animal Organism. By G. GAGLIO (*Chem. Centr.*, 1887, 1514 (from *Arch. exp. Path.*, 22, 235).—From the results of a series of respiration experiments, the author shows that carbonic oxide undergoes no oxidation when respired. He also states in opposition to Porkowsky that carbonic oxide is not oxidised by blood outside the body.

Oxalic acid dissolved in pig's blood and circulated through pig's kidneys for several hours only showed a loss of 7 per cent., a loss which occurred when oxalic acid was simply added to the kidney without circulation.

The same result was obtained in feeding experiments, the whole of the oxalic acid, with the exception of 7 to 9 per cent., being recovered from the urine.
J. P. L.

Coagulation of the Blood. L. C. WOOLDRIDGE (*Zeit. Biol.*, 24, 562—563).—In reply to the criticisms of Kruger (this vol., p. 305) Wooldridge states that he has never questioned the fact that leucocytes bring about coagulation in extravascular plasma, but he again states that as soon as they are introduced into the circulating blood they lose this property.
W. D. H.

Chromatology of Sponges. C. A. MACMUNN (*Journ. Physiol.*, 9, 1—25).—Out of the 12 species of British sponges examined, 10 (enumerated) were found to contain chlorophyll; Krukenberg and other observers have figured the dominant chlorophyll band in eight others. Probably Krukenberg (*Grundzüge einer vergleich. Physiol. der Farbstoffe*, 1884) used solutions which were too dilute to show the remaining bands, or examined only thin layers of the solutions. Lipochromes occur in nearly all sponges, and a histohæmatin in seven of the sponges examined. A pigment resembling a floridine (a class of red pigments described by Krukenberg) occurs in *Halichondria rosea*, in addition to chlorophyll, a histohæmatin, and a lipochrome. A uranidine (a class of yellow pigments described by Krukenberg) occurs in *Grantia coriacea*, in addition to chlorophyll and a lipochrome. This uranidine, like Krukenberg's aplysinofulvin (one of the five pigments of Aplysina), and others of the same class was changed by boiling to dark-green. With regard to the chlorophyll present in so many sponges, it was found to resemble plant chlorophyll very closely. The lipochrome constituent or constituents, however, reacted differently from the lipochrome constituents of plant chlorophyll, as it remained unchanged by the action of iodine in iodide of potassium, and the fractional method did not separate the chlorophyll constituents (Hansen's "chlorophyll-green" and "chlorophyll-yellow") so completely as in the case of plant chlorophyll. In these two points, it resembles enterochlorophyll (MacMunn, *Abstr.*, 1885, 1242), and proves that the chlorophyll is of purely animal origin. Microscopic search for unicellular algæ, moreover, yielded negative results. The fact that in sponges lipochromes so often accompany chlorophyll, and sometimes replace it, would go to show that the step from a lipochrome to a chlorophyll is not a great one; and it is highly probable that these pigments are concerned in the formation of fatty

matters perhaps from the waste carbonic anhydride given off during the katabolic changes in the tissues, and from the water in which they are bathed; carbohydrates are perhaps similarly formed. This would coincide with the views of Schunck (*Brit. Assoc. Rep.*, 1887), who regards chlorophyll as a respiratory pigment, but probably a carbonic acid-carrier, not an oxygen-carrier. In sponges, the histohæmatin, when present, has probably the function of an oxygen-carrier.

A chart of spectra with measurements accompanies the paper.

W. D. H.

Composition of Cow's Milk. By P. VIETH (*Analyst*, 13, 46—49).—The analysis of 12,663 samples of milk, taken throughout the year direct from the railway cans upon their arrival at the dairy, showed an average of 3.82 per cent. of fat and 12.94 per cent. of total solids. In addition, 2,948 samples were taken by inspectors during the delivery of the milk to the customers. These gave a general average of 12.89 per cent. of total solids.

An investigation of the changes taking place in the milk during delivery to customers, was made by taking a sample from the can before sending it out, and also one from the small quantity of milk left in the can upon its return from its round. In 17.6 per cent. of the cases, the latter contained more fat (0.1 to 0.34 per cent.) than the former. It is not stated whether the milk was drawn off from the bottom of the can or dipped from the top.

M. J. S.

Formation of the Colouring Matter of Bile. By J. LATSCHENBERGER (*Monatsh.*, 9, 52—92).—Experiments made with horses are described in detail, and give the following results:—The colouring matter of bile is derived from the colouring matter of the blood with simultaneous elimination of a dark pigment containing iron (melanin). The decomposition takes place in the tissues as well as outside the cells. This dissociation of the hæmoglobin into pigments free from iron (chloleoglobin) and pigments containing iron, occur both in the single blood corpuscles and in the conglomerates; in the former, the rate of decomposition is irregular, which seems to depend on the varying age of the single red corpuscles. With crystallised hæmoglobin there is no difference in time required for the decomposition of single portions of the injected mass.

The results of the microscopic examination of the various preparations are shown in coloured diagrams.

N. H. M.

Influence of the Secretion of Gastric Juice on the Quantity of Chlorine in Urine. By G. STICKER (*Chem. Centr.*, 1887, 1561—1562, from *Berl. Klin. W.*, 24, 768—771).—A rich secretion of gastric juice induces transitorily a diminution of the chlorides in urine, if conditions for its retention in the stomach or its secretion from the organism are given. The hourly secretion of chlorine increases gradually and progressively after the chief meal, and slowly diminishes again after six to seven hours. With the increase of chlorine, the activity of the urine lessens, and even changes into a strongly alkaline reaction. Towards night time, a strong decrease of the secretion of chlorine takes place. From the results of the experi-

ments no direct relation between peptic digestion and secretion of phosphates in urine can be recognised. In urine which showed an alkaline reaction, a turbidity from phosphates was regularly produced after a short time. The mean acidity of the whole 24 hours' urine is no higher on days with paroxysms of excessive acidity than on normal days.

J. P. L.

Phosphates in Urine in Different Diseases. By L. VANNI and E. PONS (*Chem. Centr.*, 1887, 1526, from *Ann. Chim. Farm.*, **87**, 259—268).—The authors advance the following conclusion with all reserve:—As a general rule, the amount of phosphate secreted in the urine diminishes in diseases of the brain and spinal cord, and frequently diminishes in cases of neurosis.

J. P. L.

Urine Reaction. By ADUCCO (*Arch. Pharm.* [3] **25**, 931, from *Ann. Chim. Farm.*, 1887, 369).—From experiments made on dogs which were compelled to run until exhausted by means of specially constructed apparatus, it was found that as the fatigue increased, the originally acid urine became gradually less acid, neutral and finally alkaline. During rest, the reverse progress went on. The alkaline reaction was caused by the presence of carbonates of the fixed alkalis and of ammonia, the relative amounts of which were, however, not constant. These carbonates are the products of reactions proceeding in the tissues, and it must be concluded that during production of fatigue, such substances more especially are used up as yield carbonic anhydride. The amount of urea present in the urine during the period of fatigue is decidedly less than before or after that period.

J. T.

Physiological Action of Alkalis and Alkaline Earths. By CRUCI (*Arch. Pharm.* [3], **25**, 931, from *Ann. Chim. Farm.*, 1887, 353).—Both the alkalis and the alkaline earths increase the blood pressure and the power of the heart, and make the pulse slower but fuller and stronger, hence are stimulants of the circulatory organs. Although the symptoms are uniform, the mechanism affected by the various elements differs considerably. Potassium, rubidium, and caesium directly affect the muscular apparatus, sodium and magnesium act on the nerve elements, lithium, barium, calcium, and strontium act in both ways. These considerations show that the alkalis and alkaline earths act as stimulants on the circulatory system; this is the more remarkable when it is remembered that the acids in general, and also the oxides of the remaining metals, exert a more or less paralytic action on that system.

J. T.

Antiseptic Properties of α -Naphthol. By J. MAXIMOVITCH (*Compt. rend.*, **106**, 366—368).— α -Naphthol is insoluble in cold water, but water at 70° dissolves 0.04 per cent. Alcohol of 40 per cent. dissolves 10 grams of α -naphthol per litre. The quantity required to prevent the development of microbes varies from 0.01 to 0.04 per cent., according to the nature of the microbe and the nidus. α -Naphthol has only one-third the poisonous action of β -naphthol, and only one seven-hundredth of that of mercuric iodide. The fatal dose

for a man of 65 kilos. would be about 585 grams; if administered by subcutaneous injection the dose would be less.

α -Naphthol is superior to β -naphthol by reason of its greater antiseptic properties and its feeblar toxic action. C. H. B.

Poisoning by Carbonic Oxide. By N. GREHANT (*Compt. rend.*, **106**, 289).—The blood absorbs carbonic oxide from an atmosphere containing only 0.02 per cent. of the gas. If the atmosphere contains 0.1 per cent. of carbonic oxide, half the hæmoglobin in the blood will combine with this gas. 100 c.c. of the blood of a dog poisoned by an atmosphere containing 0.1 per cent. of carbonic oxide contained the following gases:—

	Normal.	Poisoned.
Carbonic anhydride....	47.0 c.c.	50.0 c.c.
Oxygen.....	27.0 „	14.2 „
Nitrogen.....	1.5 „	1.5 „

On treating the poisoned blood with acetic acid at 100°, it evolved 14.4 c.c. of carbonic oxide.

The analysis of the gases from the blood is of great value in supposed cases of fatal poisoning by carbonic oxide. C. H. B.

Toxic Action of Bases produced by Alcoholic Fermentation. By R. WURTZ (*Compt. rend.*, **106**, 363—364).—The base, $C_7H_{10}N_2$, isolated by Morin (this vol., p. 572) exerts a moderate toxic action, and produces general stupefaction and reduced sensibility, with frequent micturition and dilatation of the pupil, which becomes insensitive to light. These symptoms are followed by coma and death. When administered to a rabbit by subcutaneous injection, the fatal dose is 1 gram per kilo. C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

New Lactic Acid Ferment occurring in Malt Wort. By P. LINDNER (*Chem. Centr.*, 1887, 1507, from *Centr. Bakteriol.*, 2, 340—342).—Cultivations of this sarcina formed organisms which behave similarly to *pediococcus* from beer. In neutral malt extract, it produces a sediment and cloudiness as well as a strong acid reaction after cultivation for 24 hours at 41°. The acid is lactic. It also changes the colour of the nutrient solution. The organism does not grow actively on potato, only a thin, microscopical film being formed. It grows very well on gelatin in the absence of air.

Although most of the sarcina isolated from beer have the power of forming lactic acid, none possess it to such a degree as this organism isolated from malt wort. The author provisionally calls it *Pediococcus acidi lactici*.
J. P. L.

Influence of Certain Rays of the Solar Spectrum on Root Absorption and on the Growth of Plants. By A. B. GRIFFITHS and MRS. GRIFFITHS (*Proc. Roy. Soc. Edin.*, 123, 125—129).—Mustard and bean plants grown in calcareous soil, to which had been added a definite amount of ferrous sulphate, were exposed daily to various portions of the solar spectrum. Incineration of the plants showed that the greatest amount of ferric oxide was contained in those exposed to the yellow-green rays D—E, under the influence of which rays also the greatest amount of oxygen is evolved. Examination of the plant for sulphur as representing the albuminoids, which must have derived their sulphur from the ferrous sulphate, showed that the maximum of albuminoids was attained under the influence of the rays D—E. E. W. P.

Plants Free from Chlorophyll acting like Chlorophyll-containing Plants. By F. HUPPE (*Chem. Centr.*, 1887, 1512, from *Ntf. Vers. zu Wiesbaden*, 60, 244—245).—From researches on the biology of bacteria, it appears that the qualitative differences which exist between bacteria and other plants can be referred, as regards their function, to some common origin. There is sufficient evidence to show that so far as the action of light is concerned, gradation exists between functionally undifferentiated protoplasm and ordinary chlorophyll.

The author corroborates Heraeus's statement that a nitrifying organism exists which can synthesise carbohydrates from carbonic anhydride.

The assimilation of carbonic anhydride does not therefore appear to be dependent necessarily on a specially differentiated part of protoplasm like chlorophyll. J. P. L.

Respiration of Yeast Cells at Different Temperatures. By GRÉHANT and QUINQUAUD (*Compt. rend.*, 106, 609—610).—The amount of carbonic anhydride evolved and of oxygen absorbed by yeast cells in pure water in contact with a known volume of air was determined at different temperatures. The total amount of carbonic anhydride produced and of oxygen absorbed increases with rise of temperature from 0° to 46·3°, and the ratio of carbonic anhydride to oxygen also increases. It follows that the respiration of yeast is not analogous to that of mushrooms or of plants containing chlorophyll, since, according to Bonnier and Mangin, the ratio of carbonic anhydride to oxygen does not vary with the temperature in these cases.

C. H. B.

Presence of Saccharose in Unripe Potatoes. By E. SCHULZE and T. SELIWANOFF (*Landw. Versuchs-Stat.*, 1887, 403—407).—When the unripe tubers are dried and extracted with 90 per cent. alcohol, an extract is obtained which yields a saccharate with strontium hydroxide. The saccharose from this saccharate the authors show is identical with ordinary cane-sugar. H. Müller (*Landw. Jahrbuch.*, 1882, 774) considered that saccharose was an intermediate product between starch and glucose, and it is contended that the research now published supports this theory.

E. W. P.

Detection of Saccharose in Vegetable Substances. By E. SCHULZE (*Landw. Versuchs-Stat.*, 1887, 408—413).—Employing the strontium process, the author has obtained saccharose from the etiolated shoots of potato tubers, as also from the pollen of *Pinus sylvestris*, carrots, and the leaves of the grape vines. It appears that the strontium precipitate in addition to saccharose contains mellitose and β -galactan; mellitose and saccharose are readily distinguishable by their crystals, as also by the formation of invertin by the one, and the production of mucic acid by oxidation of mellitose. To obtain saccharose in a crystalline form, when mixed with mellitose and galactose, it is recommended to evaporate the solution to a syrup, and then extract with hot alcohol, and after filtration to allow crystallisation to take place slowly.
E. W. P.

Composition of Etiolated Potato Sprouts. By T. SELIWANOFF (*Landw. Versuchs-Stat.*, 1887, 414—417).—In the dry etiolated sprouts were found 3·45 per cent. of saccharose as well as asparagine and glucose; the amount of asparagine was 2·95 per cent. on the dry substance, and the albuminoids amounted to 18·56 per cent.

E. W. P.

Action of Ether on Plant-life. By G. BRENSTEIN (*Arch. Pharm.* [3], 25, 918—924).—An atmosphere saturated with ether kills barley and wheat sprouts within 30 minutes. Five minutes' exposure affected the plants, the tips of the leaves, consequently the oldest portions, being first killed; whilst the basal portions of the leaves, and therefore the youngest parts, resisted longest. Experiments made with portions of the plant *Elodea canadensis* showed that five minutes' exposure to the ether atmosphere sufficed to kill the plant; the bicellular leaf texture of this plant seems to be more permeable to ether than are the leaves of wheat and barley.
J. T.

Aluminium as a Natural Constituent of Wheat Flour. By W. C. YOUNG (*Analyst*, 13, 5—6).—The author confirms the statement of Yoshida (*Trans.*, 1887, 748) as to the occurrence of a minute quantity of aluminium in wheat, and shows that practically the whole of it is associated with the gluten. A sample of the best Vienna flour gave 0·0075 per cent. of aluminium phosphate. The gluten from 250 grams of this flour was dissolved in acetic acid to purify it, and the solution yielded aluminium phosphate amounting to 0·0074 per 100 of flour.

M. J. S.

General Conditions favourable to the Absorption of Atmospheric Nitrogen by Vegetable Soils. By BERTHELOT (*Compt. rend.*, 106, 569—574).—The author has previously shown that soil absorbs nitrogen directly from the atmosphere, the absorption taking place under the influence of minute organisms. Oxygen must be present as well as nitrogen, since in absence of the former the anaerobic organisms increase, and a low form of green vegetation grows on the surface of the soil. These either actually destroy the aerobic organisms to which the absorption of nitrogen is due, or they remove the oxygen which is essential to their existence. The anaerobic organisms indeed actually cause a certain loss of nitrogen, pro-

bably by reduction. The porosity of the soil is essential in the highest degree, and it should contain not less than 2 per cent. and not more than 15 per cent. of water. With a higher proportion, the soil loses its porosity, especially if it is continually wet without alternating periods of dryness. Nitrification will not take place in dry soils, hence it follows that the two processes are not analogous. The temperature should not be below 10° nor above 50° . A soil which is not bearing a crop loses its power of absorbing any further quantity of nitrogen after a certain time. C. H. B.

Natural and Artificial Manures. By W. I. MACADAM (*J. Soc. Chem. Ind.*, **7**, 79—100).—A complete review of manures, both natural and artificial, with numerous analyses, giving the composition of the different manures. D. B.

Analytical Chemistry.

Simplified Chromometer for Comparison of Moderately Deep Tints. By C. H. RIDSDALE (*J. Soc. Chem. Ind.*, **7**, 70—73).—Three graduated glass comparison tubes are suspended as near each other as possible through a perforated strip of wood, supported at each end by a thick glass rod, terminating at the lower extremity in the base board. The centre tube containing the standard is sealed at the bottom, whilst the two side-tubes each have a $\frac{3}{16}$ hole in them. In all three is a small enamel glass cylinder, the top of which is the zero line, and the graduation continues upwards. A grip arrangement holding three test-tubes is clamped on the two glass supports. These slide easily over the comparison tubes, the tops when in their lowest position reaching to the zero mark of the graduated tubes. The process of comparison is as follows:—Fill the centre tube up to a certain mark with solution of standard depth of tint, pour the solution to be compared into one of the side-tubes, when it will immediately run into the test-tube beneath; when this is nearly full, look right down the two comparison tubes and raise the test-tube containing the solution to be compared, until the depth of tint is equal to that of the standard. Then read off the number of divisions required and calculate:—

$$\frac{\text{Number div. stan.} \times \text{per cent. stan.}}{\text{Number div. sol. to be tested}} = \text{per cent. sought.}$$

The author has used this apparatus chiefly for testing carbon in steel by the Eggertz colour method. D. B.

Behaviour of Congo-red towards some Acids and Salts.
By E. BRÜCKE (*Monatsh.*, **9**, 31—41; compare *Abstr.*, 1887, 986;

this vol., p. 381).—It was previously shown that carbonic anhydride colours Congo-red purple-violet; boric acid also colours it violet; with salicylic acid, a blue or slightly violet colour is obtained. Arsenious acid seems to have no action on it. The blue colour obtained by the action of acids on Congo-red is insoluble in water, and can be separated by filtration. When an aqueous Congo-red solution is treated with sufficient acid to produce a violet colour and then heated at 50° to 60°, the solution becomes purple and then red; on cooling, the original violet colour returns. This change of colour does not take place in presence of an excess of acid, except in the case of boric acid.

When so much acid is added to a solution of Congo-red that the latter becomes just blue, the addition of an acid tartrate or acetate produces a violet or red colour; more or less acid must be added to bring back the blue colour, according to the amount and nature of the salt. Congo-red is therefore unsuitable as an indicator in organic and inorganic analysis.

Congo-red can be used to show the presence of small amounts of acids in fats; an aqueous solution shaken with rancid oil becomes at once bluish-violet. When butyric acid is added to Congo-red dissolved in water, the latter becomes blue from the butyric acid dissolved; on boiling, the butyric acid takes up all the colour, leaving the aqueous solution colourless. An alcoholic solution of Congo-red is not changed by butyric or oleic acids.

Glycerol, even when containing sufficient hydrochloric acid to slightly redden litmus, will bring back the red colour of Congo-red previously made blue with a little hydrochloric acid.

The changes of colour produced by several salts are also described.

N. H. M.

Volumetric Estimation of Iodine in the Presence of Chlorine and Bromine. By N. McCULLOCH (*Chem. News*, **57**, 135—136).—By the following method, iodine may be estimated in the presence of bromine and chlorine without previous removal of the latter elements (compare this vol., p. 526). The solution containing the chloride, bromide, and iodide is mixed with its own bulk of strong hydrochloric acid, and 20 to 30 fluid grains of chloroform; standardised permanganate is dropped in, with agitation, until the iodine colour at first produced in the chloroform is again discharged owing to the formation of colourless iodine monochloride. Iodine bromide in strong solution colours the chloroform faint yellowish-pink, which cannot however be mistaken for the iodine coloration. The process cannot be employed in the presence of free hydrogen bromide and cyanide; the presence of the latter causes high results.

D. A. L.

Detection of Iodine in Urine. By C. SCHWARZ (*Arch. Pharm.* [3], **25**, 1061, from *Pharm. Zeit.*, **32**, 631).—The following method succeeds perfectly without previous concentration of the urine:—10 c.c. of urine is mixed with 2 c.c. of dilute sulphuric acid (1 : 5), with 5 drops of a 1 per cent. starch solution freshly prepared, and the whole well shaken; to the mixture is now added, drop by drop, a 1 per cent. potassium nitrite solution, when the characteristic violet or blue iodine colour appears immediately, and as quickly disappears

on adding a drop or two of decinormal sodium thiosulphate solution. More delicate still is the carbon bisulphide test when made under similar conditions; the urine to which a little bisulphide has been added must be vigorously shaken after the addition of each single drop of nitrite. Numerous urines examined have invariably given positive results whether the iodine has been applied internally or externally, and whatever compound has been employed. J. T.

Estimation of Active Oxygen by means of Tetramethylparaphenylenediamine. By C. WURSTER (*Ber.*, 21, 921—924).—The property of tetramethylparaphenylenediamine to yield a blue colour when oxidised with one atomic proportion of oxygen, and to form a colourless compound when further oxidised with six atomic proportions, can be employed as a means of estimating approximately the oxidising power of plant fluids, saliva, &c. Test-papers are used, and the colour produced by the action of one or two drops of the liquid on one of these is compared with a colour scale consisting of eight shades of colour, whose values in terms of "active" oxygen are estimated from the titre of the iodine solutions which produce similar colours on the "tetra-paper." The oxidising power of air can be estimated in like manner, by drawing a known volume of air through a tube closed at one end with a piece of "tetra-paper" moistened with dilute glycerol. W. P. W.

Determination of Sulphur in Oils. By A. H. ALLEN (*Analyst*, 13, 43—45).—The oil, a blast-furnace creosote oil containing 0.088 per cent. of sulphur, was mixed with purified methylated spirit (5 grams of oil to 45 of spirit), and the mixture after saturation with solid ammonium carbonate was burnt in a lamp, fitted by a bung into the wider end of a curved adapter. The small end of the adapter was connected with a tube bent downwards at a right angle, and passing nearly to the bottom of a wider tube (the glass jacket of a Liebig's condenser) filled with wetted glass balls. The lower end of this was furnished with a glass stopcock for drawing off the condensed liquid. The upper tubulus was connected with an aspirator. For working on rape oil, an equal weight of "kerosine" was used as diluent, and the ammonium carbonate was in this case suspended above the flame in a porcelain crucible. A sample of rape oil was found to contain 0.017 per cent. of sulphur. The ammonium sulphite in the condensed liquid was oxidised with bromine before precipitating with barium chloride. M. J. S.

Ferric Ferricyanide as a Reagent for Detecting Traces of Reducing Gases. By CRUM BROWN (*Proc. Roy. Soc. Edin.*, 124, 419).—The brown solution obtained when ferric chloride and potassium ferricyanide are mixed, and which contains ferric ferricyanide, is absorbed by strips of filter paper; these test-papers become blue in the presence of reducing gases, such as sulphurous anhydride, hydrogen sulphide, &c. As nitrous fumes also blue the test-papers, traces of them can be detected by the additional use of iodised starch-paper. E. W. P.

Kjeldahl's Method of Estimating Nitrogen. By R. MELDOLA and E. R. MORITZ (*J. Soc. Chem. Ind.*, **7**, 63).—As this process, especially when applied to the determination of minute quantities of nitrogen, requires the use of pure sulphuric acid, the authors recommend a method by which the acid may be freed from nitrogenous impurity. This is based on the well-known decomposition of ammonia by nitrous acid, the authors being of opinion that the traces of nitrogen found in impure sulphuric acid represent small quantities of ammonium sulphate. About 0.05 gram of potassium nitrite is added to 10 c.c. of sulphuric acid, and the mixture heated to expel the excess of nitrous acid. D. B.

Determination of Vanadium in the Presence of Chromium, Aluminium, and Phosphorus. By C. H. RIDSDALE (*J. Soc. Chem. Ind.*, **7**, 73—77).—After thoroughly examining all the best methods of estimating vanadium, the author found Lindemann's process (*Chem. News*, 1883, January 5) to be the most rapid and trustworthy. He has applied this method, in conjunction with a process devised by him for the estimation of other substances, to the analysis of vanadium in slag. The mode of procedure is described in detail in the original paper. D. B.

Estimation of Reduced Phosphates. By V. DIRCKS and F. WERENSKIOLD (*Landw. Versuchs-Stat.*, 1887, 425—453).—The authors have put to the proof the various processes employed for the estimation and separation of tricalcium from mono- and di-calcium phosphates, namely, the various modifications of the ammonium citrate methods. They find that although none of the methods give a really satisfactory and exact result, Petermann's process is perhaps the most trustworthy. E. W. P.

Volumetric Estimation of Boric Acid. By H. WILL (*Arch. Pharm.* [3], **25**, 1101—1113).—A rapid and fairly accurate estimation of free boric acid can be made by titration with a standard baryta solution, which is added to the solution of the acid until the turbidity appearing at first is completely and exactly removed. The amount of barium hydroxide used is exactly double the equivalent of the boric acid present, according to the equation $4\text{H}_3\text{BO}_3 + \text{Ba}(\text{HO})_2 = \text{BaB}_4\text{O}_7 + 7\text{H}_2\text{O}$. Schwarz has recently shown in the *Pharm. Zeit.* that the boric acid set free from borax by nitric acid does not affect Congo-red, whilst the slightest excess of nitric acid produces a blue-violet tint, and on this has based an obvious method for estimating the amount of acid in the borax. The boric acid thus set free can also be determined by titration with baryta-water as above, or ethyl or methyl-orange may be substituted for the Congo-red, and hydrochloric acid may be used to decompose the borax. A mixture of free boric acid and borax solution can be dealt with by a combination of the two methods, that is, by first titrating with standard acid, and then titrating the total boric acid with baryta-water. Instead of first setting free the acid, a solution of pure borax can be titrated directly by baryta solution, but only half the amount of standard solution is

now required, since the equivalent amount of sodium hydroxide set free replaces the other half of baryta.

In the presence of borax, chlorides can be estimated directly by means of silver nitrate, using potassium chromate as indicator; free boric acid interferes with the reaction in this case; the free acid is first determined by means of baryta solution; then normal soda solution equivalent to at least half the baryta solution employed is added, and then dilute sulphuric acid until neutral; the chlorides can now be directly estimated. The addition of soda solution may be omitted when estimating chlorides in the presence of little free boric acid and much borax just as in the presence of borax only. Of course, the chlorides and boric acid can be determined in separate portions, and can be directly titrated in the former after neutralisation by means of soda solution.

Boric acid in presence of sulphates is estimated by the aid of phenacetolin as an indicator. To the solution of boric acid and sulphates, two drops of an alcoholic solution of the indicator are added, and then standard baryta solution until a faint yellow tint appears; normal hydrochloric acid is now added until a faint rose tint becomes decided rose colour, the corresponding amount of baryta solution is deducted from the original amount taken, and the remainder indicates the boric acid. A further addition of hydrochloric acid until the colour changes from rose to yellow with the last drop, serves as a control estimation; the acid thus taken being equivalent to the baryta combined with the boric acid. Halving the baryta and calculating the equivalent boric acid, this should agree with the amount first formed. Sulphates of the alkalis and of the alkaline earths, excepting magnesia, may be present. A little practice is required to get the rose colour accurately, and it is found better to use normal acid rather than a weaker one. For the estimation of borax in the presence of sulphates, Schwarz's method can be directly applied. J. T.

Separation of Barium, Strontium, and Calcium. By A. RUSSMANN (*Chem. Centr.*, 1887, 1446—1447.—*Frerich's Method*).—By using the potassium chromate method for a barium salt alone, approximately correct results are obtained, but for mixtures in which barium and strontium are to be separated there should not be (1) more than 15 parts of strontium to 50 parts of barium, otherwise strontium will be precipitated as chromate; (2) nor more than 0.5 to 1 per cent. of barium and strontium in the solution. Calcium, if it is present, does not influence the precipitation of the barium. On ignition, some of the chromate is reduced to chromium oxide by the filter-paper.

Volumetric Estimation of Barium in Chromate of Barium.—None of the methods give exact results, because the hydrochloric acid used always decomposes some of the iodide of potassium even if the acid is only acting for a short time. The best results were obtained by dissolving the precipitated chromate in weak hydrochloric acid, adding the iodide of potassium, and immediately titrating after dilution. Better and quicker results are obtained by this method than by Crismer's method (*Ber.*, 17, 642).

Diehl's Method (*J. pr. Chem.*, 79, 430).—This method depends on

the solubility of calcium sulphate in sodium thiosulphate. The barium sulphate carries down an important quantity of calcium sulphate which cannot be dissolved even by long-continued digestion with warm sodium thiosulphate. Barium sulphate is, however, quite insoluble in the sodium thiosulphate. Besides this objection, the sulphur which separates, and agglomerates when the estimation of the lime is proceeded with, encloses some lime, or, again, a part of the lime may be converted into sulphate.

*Separation of Barium and Calcium with Sulphuric Acid (1 : 300).—*This process gives good results both when there is much calcium and little barium, and when there is much barium (100 parts) and little calcium (1 part). Lime is never precipitated.

Sidersky's Method (Abstr., 1883, 509) (*Ammonium Sulphate and Oxalate*).—Sidersky's second method gives good results, namely, precipitation of strontium and calcium salts with ammonium sulphate and oxalate in a solution acidified with hydrochloric acid. Strontium sulphate only is precipitated if the acid used contains not less than 8.5 per cent. of HCl. Calcium and barium may also be satisfactorily separated by this process.

*Bloxam's Method for Detecting Calcium in Presence of Strontium (Calcium Ammonium Arsenate, Abstr., 1886, 920).—*The method is very useful as a qualitative test; 1 part of calcium in presence of 500 parts of strontium can be readily detected. For quantitative determinations the process is inexact.

Fleischer's Method.—The process is useful for solutions in which barium and calcium are present but no magnesium.

Leison's Method.—The volumetric estimation of oxalates of the alkaline earths by the use of potassium permanganate in acid solution gives good results. It is quicker, however, to ignite the precipitate.

J. P. L.

Separation of Copper and Arsenic, and their Estimation in a Case of Poisoning. By P. GUCCI (*Chem. Centr.*, 1887, 1528, from *Atti della Soc. Toscana di Sc. Naturali*, 5, 287—289).—If copper and arsenic, occurring together in intestinal contents, be precipitated as sulphides after treatment of the intestinal matter with potassium chlorate and hydrochloric acid, their separation by means of alkali sulphides is unsatisfactory. The copper sulphide is in such a fine state of division that it cannot be separated by filtration, and an important amount also remains in solution.

The author treats the washed and dried sulphides with fuming nitric acid, evaporates to dryness, and repeats the treatment. The final residue is then melted with soda and potassium nitrate. The melt is dissolved in water and nitric acid, the copper precipitated with potash, and weighed as oxide. From the filtrate, the arsenic is precipitated either as ammonio-magnesian arsenate or as arsenic sulphide.

J. P. L.

Detection of Mercury in Urine. By K. ALT (*Arch. Pharm.* [3], 25, 969—970, from *Centr. Med. Wiss.*).—The urine is acidified with hydrochloric acid, and in it is immersed a piece of tinsel (a zinc-copper alloy) about 8 × 4 cm., fastened to the cork of the vessel.

The liquid is heated at 60° for half an hour, and then allowed to remain for 15 hours, so that the free mercury collects on the upper surface of the tinsel. The latter is taken out, washed with water, dried with alcohol and ether, carefully folded, and placed in a test-tube, in which it is heated for half a minute, during which a trace of iodine is brought into the tube; the presence of mercury is immediately shown by the appearance of a film of iodide on the tube; 0.016 mgrm. of mercuric chloride can thus be detected in 100 c.c. of urine, whilst the limit of Fürbringer's test is 0.2 mgrm., and that of Müller's is 0.06 mgrm. J. T.

Estimation of Iron. By C. SCHACHT (*Arch. Pharm.* [3], 25, 906—910).—In a well-stoppered flask, 1 gram of *ferrum oxydatum saccharat. solubile* is covered with 5 c.c. of hydrochloric of 1.12 sp. gr.; after standing 10 minutes, 50 c.c. of water and 0.5 gram of potassium iodide are added, and the flask is set in a warm place for an hour, when the free iodine is titrated by means of decinormal sodium thiosulphate solution. To estimate the iron in *ferrum carbonic. saccharat.*, 0.5 gram is heated with 5 c.c. of dilute sulphuric acid until completely dissolved. After cooling, permanganate solution is added to the clear solution just to faintly tint it, then 1 gram of potassium iodide as above. By this short method fairly concordant results were obtained with numerous pharmaceutical preparations of iron. J. T.

Aluminium in Wheat. By A. H. ALLEN (*Analyst*, 13, 41—43).—From the statements of various food-analysts, it seems that aluminium in minute proportions is a normal constituent of wheat, the amount corresponding with about 8 grains of alum in the 4-lb. loaf. A method of determining the alumina present, otherwise than as silicate, consists in dissolving the starch by means of malt extract, fermenting the solution with yeast, acidifying with nitric acid, filtering, evaporating, and igniting the residue, then precipitating the alumina as phosphate in the usual way. M. J. S.

Separation of Iron, Nickel, Cobalt, Manganese, Zinc, and Aluminium. By T. MOORE (*Chem. News*, 57, 125).—The present process is a modification of the one previously described (Abstr., 1887, 1141). Excess of solid sodium hydrogen carbonate is mixed with the cold, concentrated, and slightly acid solution, potassium cyanide is then added until the precipitate is dissolved, and the whole heated until the solution assumes the yellow colour of the ferrocyanide, and is perfectly clear; when, however, alumina is present, the solution remains somewhat turbid, but is clarified by a few drops of potash. To separate nickel from iron, this solution when cool is mixed with a large excess of moderately strong potassium hydroxide, and treated with chlorine until the nickel hydroxide is completely converted into the peroxide, which is separated and treated in the usual manner for electrolytic deposition.

Alumina may be separated from iron, nickel, and cobalt by boiling the clear solution of the mixed ferrocyanides with ammonium chloride. To separate manganese from iron, nickel, and cobalt, the above clear

solution is best precipitated by means of hydrogen sulphide, the manganese is rapidly and completely precipitated as sulphide, and is easily washed, &c. When, however, the clear solution is boiled with ammonium sulphide until ammonia ceases to be evolved, zinc sulphide alone is precipitated, and, therefore, this forms a ready method of separating zinc from iron, nickel, and cobalt. D. A. L.

Separating Tin from Antimony and Estimation of these Metals in Siliceous Slags and Alloys. By H. N. WARREN (*Chem. News*, 57, 124—125).—The powdered slag is dissolved in a mixture of equal parts of hydrochloric and hydrofluoric acids, the solution filtered, heated, saturated with hydrogen sulphide, and the precipitate boiled with sodium hydroxide. The sulphides of tin and antimony are then reprecipitated by means of hydrochloric acid, and decomposed with aqua regia; the solution is evaporated to a small bulk, diluted with weak hydrochloric acid, and treated with potassium ferrocyanide, until it assumes a clear, blue colour, when the solution is allowed to boil. The tin is precipitated as stannic ferrocyanide, whilst the antimony remains in solution. Both metals are then easily determined. Alloys are dissolved in aqua regia instead of the mixture of hydrogen fluoride and chloride. D. A. L.

Chloroform Testing. By G. VULPIUS (*Arch. Pharm.* [3], 25, 998—1001).—Chloroform for medicinal use should be required to pass the following test:—10 c.c. mixed with 2 c.c. of water, 2 drops of phenolphthalein solution, and 1 drop of decinormal potash solution, is shaken repeatedly in a stoppered flask which it nearly fills; the red colour should not disappear in 24 hours; and the usual test with sulphuric acid should not give a perceptible yellow colour within one day. J. T.

Estimation of Chloroform, and its Solubility in Water. By G. CHANCEL and F. PARMENTIER (*Compt. rend.*, 106, 577).—The method for the estimation of chloroform described by St. Martin (this vol., p. 570), has previously been described by the authors (*Abstr.*, 1885, 363). They find that the solubility in water decreases from 0° to 54·9°, the amount dissolved per litre varying from 9·87 to 7·75 grams. They did not obtain any saturated solution containing only 6·4 grams as stated by St. Martin. C. H. B.

Estimation of Starch. By J. N. SPENCE (*J. Soc. Chem. Ind.*, 7, 77).—Having occasion to estimate the amount of starch in pepper, the author tried Asboth's process (*Abstr.*, 1887, 868), but could not obtain constant results. Asboth recommends the addition of the baryta-water in the cold, but the author finds that by adding it to the hot solution, a better marked compound is obtained. The author also shows that the barium-compound is soluble in water, but is precipitated again by the alcohol, it is therefore not insoluble as stated. The standard baryta-water should never be below the strength capable of saturating 90 c.c. of decinormal hydrochloric acid, other-

wise it is possible to form more than one compound, the nature of each depending on the strength of the baryta-water. D. B.

Detection of Acetic Acid in Presence of Morphine. By G. S. JOHNSON (*Chem. News*, 57, 83).—An aqueous solution of morphine acetate is treated with a solution of ferric chloride, avoiding excess of acid; the morphine blue colour develops at once, but on warming gives way to the blood-red colour of ferric acetate. 1 part of morphine acetate in 870 parts of water may be detected by this means.

D. A. L.

Action of Sulphur Chloride on Oils. By T. T. P. B. WARREN (*Chem. News*, 57, 113; compare this vol., p. 199).—While examining oils or oily mixtures, the melting point, consistency, viscosity, and other properties should be noted at the various stages:—5 grams of the oil are mixed first with 2 c.c. of carbon bisulphide, then with 2 c.c. of a mixture of equal parts of carbon bisulphide and sulphur chloride, and heated; at the completion of the reaction, the volatile products are expelled, and the appearance of the mass noted. This is then transferred to the filter-tube, washed with carbon bisulphide, and the extracted matter weighed. The colour, odour, &c., of both the insoluble and soluble products will in many cases indicate what oils they are. If the extract is turbid from deposited sulphur, the oil-mass, after it has been weighed, is treated with ether saturated with sulphur, and the weight of any residual sulphur is then deducted from the weight of the oil. The author gives an example of his mode of dealing with a mixture of two oils, both yielding solid products with sulphur chloride (*loc. cit.*), and points out difficulties arising from the solvent action of one oil on another. He has found arachis oil largely adulterated with cotton-seed oil.

D. A. L.

Detection of Cotton-seed Oil. By E. MILLIAU (*Compt. rend.*, 106, 550—551).—If the purified fatty acids obtained from cotton-seed oil are dissolved in 3 vols. of alcohol of 90°, and boiled for some minutes with 2 c.c. of a 3 per cent. solution of silver nitrate, the latter is reduced, and the silver rises to the surface of the liquid in the form of a pasty mass. This reaction is not obtained with the fatty acids from olive oil, and is sufficiently delicate to detect 1 per cent. of cotton-seed oil in olive oil.

When the dried fatty acids from oil of sesame are mixed with an equal volume of hydrochloric acid containing sugar, a blood-red coloration is immediately produced. The fatty acids of olive oil and other oils do not give this reaction, and it will detect 1 per cent. of oil of sesame in a mixture of oils. If the test is made directly on the oils, the result is uncertain, since the aqueous liquid which runs from the olives in the process of pressing gives a similar coloration. By operating on the separated fatty acids, however, the uncertainty is removed.

C. H. B.

Estimation of Fat in Fodder. By L. BÜHRING (*Landw. Versuchs-Stat.*, 1887, 419—423).—It is advisable for the correct estimation of fat in fodders of all kinds, that the sample should be

thoroughly dried, either in a vacuum or at 100°, also that the ether should contain no water; as otherwise, carbohydrates are dissolved, which materially raise the percentage of fat. Several analyses are given to show the effect of drying.

E. W. P.

Relation between Specific Gravity, Fat, and Solids in Milk.

By P. VIETH (*Analyst*, 49—51).—Hehner and Fleischmann have published formulæ (for the latter see this vol., p. 94) by which the fat in milk can be calculated from the specific gravity and amount of total solids. With Hehner's formula, the difference between the calculated percentage of fat and that determined by extraction from a paper coil (Adams' process) is small with low percentages of fat, but considerable when the percentage of fat is large. Comparing Fleischmann's formula with the results of extraction after drying on gypsum, the differences never exceed 0.2 per cent. (above or below), and the average difference in 530 analyses was 0.02 per cent. These formulæ are only applicable where, as in cow's milk, the ash, proteïds, and sugar are in the ratio 1 : 5 : 6. In human milk the ratio is 1 : 5 : 10, and in mare's milk, 1 : 6 : 23.

M. J. S.

Action of Alcohol on Butter Fat. By C. B. COCHRAN (*Analyst*, 13, 55—57).—To test artificial butter for added tributyrates, it has been recommended to treat the sample with alcohol, and ascertain by Reichert's process whether the amount of volatile acid in the undissolved residue is less than in the original substance. Genuine butter gives, however, precisely this result. Several samples of genuine butter were treated with alcohol at 23—25°, using 10 c.c. of 90 per cent. alcohol to 1 gram. The percentage of volatile fatty acid in the undissolved residue was in every case reduced, but in no case did the distillate from 2.5 grams of the undissolved portion require less than 9 c.c. of N/10 alkali. This number is therefore accepted as the minimum for a genuine butter, after treatment with the above proportion of alcohol, and it is suggested that adulteration is more likely to be detected by applying Reichert's method to the undissolved fat than by using it on the original butter.

It is noticed that genuine butter which has been kept for some time may in Reichert's process give results falling below the standard of 12.5 c.c. of N/10 alkali for 2.5 grams of butter. In one case of a butter 10 months old, but in good preservation and palatable, only 10.5 c.c. were required.

M. J. S.

Bases in Alcoholic Liquids. By L. LINDET (*Compt. rend.*, 106, 280—283).—500—1000 c.c. of the liquid at 50° Gay-Lussac is mixed with 20 grams of strong sulphuric acid, well agitated and distilled until all alcohol and water is expelled. 0.5 gram of mercury is added, and the operation conducted exactly as in the estimation of nitrogen by Kjeldahl's process, the nitrogen of the bases being obtained in the form of ammonia. One part of base in 1,000,000 parts of alcohol can be detected, and the distillate contains no bases.

The examination of several alcoholic liquids in this way shows that the amount of ammonia per litre of liquid varies from 0.40 to

23·05 mgrms. Alcohols obtained by the fermentation of grain contain the smallest amount; the quantity in rum is much higher than in other spirits, whilst the alcohol from beetroot molasses contains a very much higher proportion than any of the others. C. H. B.

Estimation of Morphine in Opium. By A. KREMEL (*Chem. Centr.*, 1887, 1529—1530, from *Pharm. Post*, 20, 661).—5 grams of opium powder is digested with 75 c.c. of lime water for 12 hours with frequent shaking; 60 c.c. of the filtered liquid, which should not have an alkaline reaction, is mixed with 15 c.c. of ether and 4 c.c. of normal ammonia in a weighed flask. The flask is corked and the contents mixed with gentle shaking. The ether is decanted after remaining at 10—15° for 6 to 8 hours, another 5 c.c. of ether is added, and this again decanted after gentle shaking. The crystals of morphine separated with the ether are collected on a small filter. These crystals, with those remaining in the flask, are washed with 5 c.c. of water, and both finally dried at 100° and weighed.

J. P. L.

Estimation of Morphine in Opium. By E. F. TESCHEMACHER and J. D. SMITH (*Chem. News*, 57, 93—95, 103—105).—The authors review and criticise the methods recommended for the determination of the morphine in opium, and point out that those depending on the use of lime, much alcohol, or much water, are untrustworthy; in this category they include the Squibb-Flückiger method even as modified by Stillwell (*Abstr.*, 1887, 403), the Hager-Jacobsen, Merck's, the British Pharmacopœia, and other methods. It is noteworthy that any one of these methods will give concordant results when applied in the same manner to the same sample of opium, but nevertheless the results are erroneous. A small quantity of alcohol is necessary, as otherwise the morphine is precipitated in a form difficult to wash, but the quantity should not exceed 50 grains of alcohol to 200 grains of opium; the authors approve the idea suggested by Allen, of finally titrating the morphine, as this excludes errors due to adherent colouring matter, &c. Their own method is fully described, and is briefly as follows:—Exhaust 200 grains of opium with warm distilled water, concentrate steadily to a thin syrup, mix with 50 fluid grains of alcohol, sp. gr. about 0·820, and about 600 fluid grains of ether, then add 50 fluid grains of ammonia, sp. gr. 0·935, shake well, and agitate occasionally during the next 18 hours, filter, and to remove colouring matter, &c., wash first with 80 per cent. spirit saturated with morphine, then with morphinated water. Dry carefully, pulverise, digest with benzene, filter, dry, weigh, and finally titrate with standard hydrochloric acid, using litmus as indicator, &c. Benzene dissolves all other opium alkaloids except morphine and narceine, and the latter is removed in the earlier stages of this process.

D. A. L.

Estimation of Morphine in Opium. By R. WILLIAMS (*Chem. News*, 57, 134—135).—The author's experience with the processes generally employed for the estimation of morphine in opium confirms the opinion expressed by Teschemacher and Smith (preceding

Abstract). The method he now employs is similar to that described by the latter authors, except that he prefers to extract the opium with cold instead of warm water, and uses 100 instead of 50 grains of alcohol.

D. A. L.

Testing Neutral Quinine Salts. By L. SCHÄFFER (*Arch. Pharm.* [3], 25, 1041).—The oxalate test may be applied directly to those neutral quinine salts whose solubility in water is not less than that of quinine sulphate, for instance the hydrochloride, bromate, valerate. Thus a molecular quantity corresponding with 1 gram of the sulph. cryst. is weighed off and treated as described in the following Abstract. Collateral alkaloid mixtures are indicated as sharply as in the case of the sulphates, except that, as with quinine valerate, a portion of the acid is lost during heating and it becomes alkaline, when a little more passes the test.

J. T.

Estimation of Cinchonidine in Quinine Sulphate. By L. SCHÄFFER (*Arch. Pharm.* [3], 25, 1033—1041).—The ammonia method given by Kerner and Weller (Abstr., 1887, 1146) is shown to be quite fallacious, mainly owing to the readiness with which a double salt of quinine and cinchonidine sulphate is formed. Further, animal as well as vegetable fibres absorb variable quantities of the quinine alkaloids, and the use of different kinds of filter-paper may produce a difference of 1 c.c. in the amount of ammonia solution used. Glass-wool filters should be employed. The oxalate test (Abstr., 1887, 623) is slightly modified on this account. 1 gram of quinine sulph. cryst. (0.85 gram completely dried sulphate) is boiled with 35 c.c. water in a small tared flask. To this is added 0.3 gram of neutral crystallised potassium carbonate (oxalate?) in 5 c.c. water, and the solution is made up to 41.3 c.c. The flask is kept at 20° and shaken occasionally during half an hour, when its contents are filtered through glass-wool, and to 10 c.c. a drop of officinal aqueous soda is added. No turbidity appears for some minutes if the original sulphate is pure. 1 per cent. of cinchonidine may thus be missed. 1½ per cent., however, gives an immediate turbidity, and larger quantities afford a precipitate. On filtering through glass-wool after one hour, 2 per cent. or more affords an immediate turbidity or a precipitate.

J. T.

Colchicine-like Decomposition Product. By G. BAUMERT (*Arch. Pharm.* [3], 25, 911—918).—In a supposed poisoning case, the Stas-Otto method was followed, and a substance closely resembling colchicine was found, although death had occurred twenty-two months previously. Parallel reactions made with pure colchicine differed in many cases from those obtained with the extract from the body; but when an aqueous extract was exhausted as far as possible by means of chloroform, and to this was added pure colchicine, the reactions then became identical with those given by the substance obtained from the body. Brieger, however, found that the substance was a peptone and physiologically inactive. Millon's reaction confirmed this. The peptone is also distinguishable from colchicine by giving a precipitate with picric acid, and with platinum chloride.

J. T.

General and Physical Chemistry.

Spectrum of the Oxyhydrogen Flame. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **43**, 347—348).—The authors examined the third portion of the water spectrum extending into the ultra-violet. The lines fall into rhythmical groups, in which in many cases the distances between the lines measured in wave-lengths are in arithmetical progression. They find a striking resemblance between these groups and the groups A, B, and α , but no exact correspondence, as stated by Deslandres. They have found many of the lines predicted by Grünwald (Abstr., 1887, 1070). H. K. T.

Wave-lengths of two Red Lines in the Spectrum of Potassium. By H. DESLANDRES (*Compt. rend.*, **106**, 739).—By means of the electric arc and a Rutherford grating on glass, the author has determined the wave-lengths of the two potassium lines in the extreme red, and obtains for the stronger of the two the value 7663.0, and for the weaker 7696.3, D being taken as 5888.9. The mean value is 7679.65. Mascart by the same method found 7680.0, D being taken as 5888.0. C. H. B.

Ultra-violet Band-spectrum of Carbon Compounds. By H. DESLANDRES (*Compt. rend.*, **106**, 842—846).—The violet portion of the visible spectrum of carbon compounds in tubes under low pressure contains two groups of bands, the first of which is usually attributed to hydrocarbons, and is seen in the spectra of comets, whilst the second is most distinct under very low pressures, and was attributed by Ampère to carbonic oxide.

Carbonic oxide with a non-condensed spark under atmospheric pressure shows the first group only, whilst in the ultra-violet there is a faint trace of the carbon line $\lambda 2478.5$. Under very low pressures, however, this gas gives a very fine band spectrum in the ultra-violet, whilst in the visible spectrum group 1 is replaced by group 2, which is very brilliant. The ultra-violet spectrum includes, besides some bands of group 1, at least two distinct groups of bands, different in character from the visible bands, and readily distinguishable from one another. The bands in the 3rd group shade off on the more refrangible side, whilst those of the 4th group shade off in the opposite direction. Almost exactly the same spectra were obtained at low pressures with carbonic anhydride, acetylene, and cyanogen, although in the latter case the special bands of nitrogen and of cyanogen were recognisable. The exact origin of the bands was not determined. Their appearance is independent of the presence of nitrogen, and it seems probable that group 3 is due to some oxygen compound, whilst group 4 is due to the vapour of carbon only. The bands on the one hand and the lines on the other may be divided into series which,

when represented on a scale of vibration-frequency, are in arithmetical progression, and are represented by the expression $Am^2 + \alpha$, m being a whole number.

Group 3 has the same general appearance as group 2, usually attributed to carbonic oxide. The arrangement of the bands is simple, but the bands themselves are of complex structure.

Group 4 is different in appearance from any other carbon groups or nitrogen groups. It resembles the absorption-spectrum of iodine, and can be divided into five similar series, which are also in arithmetical progression. The bands are of comparatively simple structure, and are resolved into lines by two prisms of Iceland spar. Each band consists of two equal arithmetical series which are superposed on each other.

The division of the bands into series requires three successive operations, and the whole of the rays may be represented by a function of three parameters, m^2 , n^2 , p^2 , of the form—

$$f(n^2, p^2) \times m^2 + Bn^2 + \phi(p^2),$$

m , n , and p being whole numbers. The law of periods in the more general vibratory motion of a solid, and in all similar problems of periodic vibrations, can likewise be represented as a function of three parameters, m^2 , n^2 , and p^2 , which correspond with the three dimensions of space. The functions f and ϕ have not been accurately determined, but they seem to be of simple character, such as squares, inverse squares, or square roots.

C. H. B.

Spectra of Meteorites. By J. N. LOCKYER (*Proc. Roy. Soc.*, **43**, 117—156).—Observations were made on the spectra of elements and meteorites at low temperatures, namely, those of the bunsen flame, oxyhydrogen blowpipe, and vacuum discharge. The spectra were compared with those of the heavenly bodies. The following deductions are made:—The luminous phenomena of all heavenly bodies shining by their own light, with the exception of stars like the sun and Sirius, are produced by meteorites; the temperature of the meteorites in some cases is about that of the oxyhydrogen flame; the intensity of the light depends on the number of meteorites in the swarm; the main factor in the spectra produced is the ratio between the meteorites and the spaces between them; when the space is great the tenuity of the gases given off by the collisions is too great to give a luminous spectrum, later bright lines or flutings are produced, finally when the meteorites themselves are more crowded, and at a higher temperature, a continuous spectrum with dark lines will result; new stars are produced by the collision of swarms of meteorites, the lines being those of elements which give bright lines at low temperatures; the hydrogen spectrum in nebulae is due to electrical excitation, the glow of a meteorite in a vacuum giving the hydrogen or carbon spectrum according to the amount of heat applied; the production of iron meteorites with embedded stones is due to the welding of the fused iron when meteorites collide. The author represents the consecutive conditions of stars by a curve, commencing with a low temperature swarm of meteorites, which by their gravitation produce a rise of temperature up

to a certain height to afterwards decrease in temperature by radiation as the incandescent mass assumes first a vaporous and finally a solid condition. In the ascending branch are (1) nebulae (bright lines); (2) stars with bright lines; (3) stars with little absorption, bright hydrogen lines; (4) stars with bright carbon, manganese, and zinc flutings; (5) stars with line absorption; at the top of the curve are stars with hydrogen absorption. In the descending branch are (1) stars with line absorption; (2) stars with carbon absorption. The sun is situated in the descending branch, as shown by the great thickening of the potassium line due to a concentration of the sun's atmosphere by condensation.

H. K. T.

Galvanic Elements. By ROBERTS (*Dingl. polyt. J.*, **267**, 141).—The "permanganate element" is said to be free from chemical action when the circuit is broken. The solution consists of potassium permanganate, potassium dichromate, common salt, and sal-ammoniac. The negative electrode is a rod of zinc, the positive a carbon prism. The mean E.M.F. is 1·8 volts, the internal resistance 0·5 ohm. One element is sufficient to work an electric bell.

The "lead dioxide element" is prepared by mixing red lead with powdered potassium permanganate and sulphuric or hydrochloric acid. The mixture is poured into a mould containing carbon, and on solidifying forms a good porous conductor, which adheres firmly to the carbon, and has the same hardness. The electrode thus obtained is employed as a substitute for carbon with zinc and sulphuric acid, and yields a very constant current. By the application of a solution of salt and sodium dichromate still better results are obtained.

The electrolyte in the so-called "dry element" forms a thick, pasty substance prepared by mixing two saline compounds, each dissolved separately.

D. B.

Experiments with Lippmann's Capillary Electrometer. By J. H. PRATT (*Amer. J. Sci.*, **35**, 143—151).—A description of the instrument used, which is of very simple construction, is given. The results show that it may be employed for measuring low potentials, up to 0·6 or 0·7 Daniell, and therefore for comparing the E.M.F. of different batteries, if only a known fraction of the current be used. Oxygen polarisation must be avoided, and only hydrogen polarisation employed. Under these conditions, the deflection of the meniscus may be taken as proportional to the E.M.F. for very low potentials, and for potentials up to 0·9 Daniell an empirical curve will show the relation between the two. The polarisation is complete, and no appreciable current passes through the electrometer until it is charged to a potential near that at which electrolytic action begins. The capacity of the instrument is very considerable as compared with that of the quadrant electrometer.

H. C.

Aëration Currents. By C. R. A. WRIGHT and C. THOMPSON (*Proc. Roy. Soc.*, **43**, 268—273; compare *Trans.*, 1887, 672; *Abstr.*, 1887, 1008).—If different aëration (spongy and smooth platinum and gold) plates are placed above the same oxidisable metal in dilute sulphuric acid or aqueous potash, and left until a con-

stant aëration is obtained, and if they then are connected together, a current is set up, which lasts with decreasing intensity for several days, and which at starting has an electromotive force equal to the difference between the electromotive forces obtained by exposing each plate to the oxidisable metal. The passage of the current electrolyses the sulphuric acid, with the result that the aëration of the positive plate is reduced, whilst that of the negative plate is increased. If the current is interrupted for some time, the plates recover their original aëration. With silver plates in sulphuric acid, acetic acid, and aqueous ammonia, a stronger current is obtained, the silver passing into solution; moreover, the amount of silver deposited in a voltameter by the current is less than that dissolved in the cell. The difference is greater with feeble than with strong currents. If the silver is opposed to a powerful oxidising agent such as platinum in nitric acid, the current produced is stronger, but the discrepancy between the quantity of silver dissolved and that deposited remains. Other metals dissolve in the same way, thus mercury opposed to an aëration plate gives mercurous sulphate. Gold in potassic cyanide gives potassium aurocyanide. Palladium behaves in a similar manner. If platinum in chromic acid is substituted for the aëration plate, gold can be dissolved in hydrochloric acid, forming aurous chloride which subsequently decomposes.

H. K. T.

Electrical Conductivity of Sulphur. By E. DUTER (*Compt. rend.*, 106, 836—837).—Sulphur is a non-conductor at all temperatures below its boiling point, but at this temperature it is possible to pass an appreciable current through the liquid. The gold electrodes which were used became covered with a deposit which is under examination.

C. H. B.

Electrical Conductivity of Concentrated Nitric Acid. By E. BOUTY (*Compt. rend.*, 106, 654—657).—The addition of water to fuming nitric acid at first causes an increase in conductivity almost proportional to the quantity of water added, and this proportionality persists through a much wider range than the increase in conductivity resulting from the addition of nitrates. From 0.076 mol. H_2O to 1.478 mol. H_2O the mean increase in conductivity is 0.456 for $\frac{1}{2}\text{H}_2\text{O}$, the unit being the conductivity of normal nitric acid, the specific resistance of which at 0° is 4.59 ohms.

When the increase in conductivity produced by salts (6.955 per equivalent) is compared with that produced by water (0.456 per equivalent), the water is less active than the salts in the ratio of 1 : 15.25, and this ratio would be still lower if the pure acid were the basis. It would seem that the electrolyte produced by the first additions of water contains a somewhat large number of molecules of water in each molecule of electrolyte.

The addition of small quantities of dehydrating substances, such as phosphoric anhydride or sulphuric acid, to the nitric acid increases its conductivity, probably owing to the formation of complex electrolytes containing both acids.

The determinations of the conductivity of concentrated nitric acid

itself were not very satisfactory, owing to the action of the acid upon the vessels containing it, and consequent variations in resistance. Probably the electrolytic molecules are not the same with different degrees of dilution. A study of the phenomena of polarisation seems to indicate three distinct phases in the electrolysis, namely, the phase of the formation of the electrolyte corresponding with a composition represented by the formula $N_2O_5, 4H_2O$, the E.M.F. of polarisation being 0.05 to 0.2 volt, and the increase in conductivity per equivalent of water 0.456, whilst the principal product at the cathode is nitrogen peroxide; (2) the *phase of dissociation* extending somewhat beyond the point of maximum conductivity, with an E.M.F. of polarisation of 0.6 to 0.9 volt, the product at the cathode being a complex mixture containing nitrous acid; (3) the phase extending from the point of maximum conductivity to high degrees of dilution, the E.M.F. of polarisation being from 1.6 to 1.8 volt, whilst hydrogen is the only product at the cathode. C. H. B.

Influence of the Composition of Glass on the Depression-phenomena of Thermometers. By R. WEBER (*Ber.*, 21, 1086—1096).—Tables are given showing the composition of various kinds of glass, and the depression which took place after various lengths of time. The results show that the quantity of silica present does not affect the depression, nor has the quantity of lime, which varies from 10 to 15 per cent., any appreciable effect. Neither a large amount of lime nor of silica can counteract the injurious effect caused by the presence of both potash and soda. The quantity of alumina has relatively little effect on the depression, but its presence is of use in promoting the liquefaction and thorough melting of the glass.

F. S. K.

Conduction of Heat in Liquids. By C. CHREE (*Proc. Roy. Soc.*, 43, 30—48).—A flat-bottomed dish is supported just in contact with the surface of the liquid, and into this, water at about 75° is poured, the temperature at a known depth below the surface being then ascertained at intervals by measuring the resistance of a platinum wire suspended horizontally 2.6 cm. beneath the bottom of the dish. From these measurements, the conductivity is deduced. Two series of experiments are distinguished; in the first, the water in the dish was syphoned off after a certain interval of time had elapsed; in the second, it was allowed to remain in the dish until the end of the experiment. In the first series, the conductivities measured are, the units being centimetre and minute—

For water at 18° = 0.0747.

For sulphuric acid, sp. gr. 1.054, at 20.5° = 0.0759.

For sp. gr. 1.10, at 20 $\frac{1}{4}$ ° = 0.0767.

For sp. gr. 1.14, at 19 $\frac{3}{4}$ ° = 0.0765.

For sp. gr. 1.18, at 21° = 0.0778.

From which it appears that the presence of a very considerable quantity of sulphuric acid produces an extremely small change in the conductivity for heat of water.

For carbon bisulphide at $15^{\circ} = 0.0322$.

For methylated spirit at $19.5^{\circ} = 0.0354$.

For paraffin oil at $19^{\circ} = 0.0264$.

The method and theory are not sufficiently accurate to allow of any value being attached to the third significant figure in the above.

The results in the second series were—

For water at $195^{\circ} = 0.0815$.

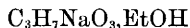
For methylated spirit at $18^{\circ} = 0.0346$.

For paraffin oil at $20^{\circ} = 0.0273$.

For turpentine oil at $18^{\circ} = 0.0189$.

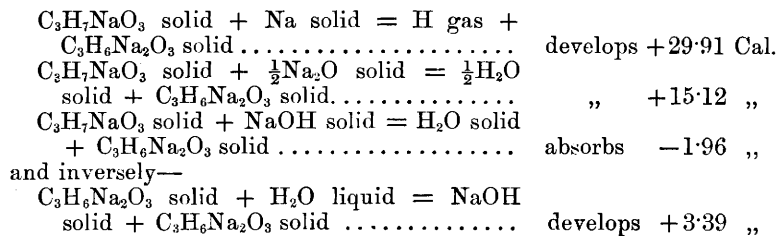
The results on the whole agree with Weber's (*Ann. Phys. Chem.* [2], 10, 103, 304, and 472). H. C.

Bibasic Glyceroxides. By DE FORCRAND (*Compt. rend.*, 106, 665—667, and 746—749).—When sodium ethoxide and monosodium glyceroxide in molecular proportions are heated together for some time in presence of an excess of alcohol, and the liquid evaporated to dryness in a current of hydrogen at a temperature not exceeding 180° , the product contains 29.23—29.86 per cent. of sodium, and hence only about half the sodium in the ethoxide combines with the glycerol. If, however, evaporation takes place at 180 — 190° , decomposition is practically complete. Below 100° , the compound



is formed; at 100 — 105° , or even 120° in dry hydrogen, the product is $\text{C}_3\text{H}_7\text{NaO}_3, \text{EtONa}$; at 180 — 190° the bibasic glyceroxide, $\text{C}_3\text{H}_6\text{Na}_2\text{O}_3$, is obtained. Potassium methoxide and monopotassium glyceroxide do not react at 180° even after several hours.

The heat of solution of *disodium glyceroxide*, $\text{C}_3\text{H}_6\text{Na}_2\text{O}_3$, at 10° is +14.48 Cal.



The last result explains the instability of the compound in moist air. In the case of monosodium glyceroxide, this reaction is endothermic, and hence the compound is much more stable, and can even exist in solution in a partially dissociated condition. The reaction $\text{C}_3\text{H}_7\text{NaO}_3$ solid + EtONa solid = $\text{C}_3\text{H}_6\text{Na}_2\text{O}_3$ solid + EtOH liquid absorbs -2.08 Cal., is endothermic for the solid compounds, but becomes possible under the complex conditions of dissociation resulting from the action of heat. The following result, $\text{C}_3\text{H}_7\text{NaO}_3, \text{EtOH}$ solid + EtONa dissolved in $n\text{EtOH}$ liquid = $\text{C}_3\text{H}_6\text{Na}_2\text{O}_3$ solid +

$(n + 2)\text{EtOH}$ liquid, absorbs -16.64 Cal., explains the fact that disodium glyceroxide is only formed at a high temperature. The corresponding reaction for the monobasic glyceroxide is exothermic, and this compound is formed at the ordinary temperature.

C_3 (diamond) + H_2 gas + Na_2 solid + O_3 gas = $\text{C}_3\text{H}_5\text{Na}_2\text{O}_3$ solid, develops $+239.62$ Cal.

The author was unable to obtain any alcoholate of disodium glyceroxide. The residue at 120° is shown by its stability in a vacuum at 105° , and its heat of solution ($+13.52$ Cal. at 10°) to be the compound $\text{C}_3\text{H}_7\text{NaO}_3, \text{EtONa}$.

The heat of formation of this compound from its proximate constituents is $+1.34$ Cal., and in the production of disodium glyceroxide it is first formed with development of heat, but at a higher temperature decomposes with absorption of -3.5 Cal.

The heat developed by the action of a second molecule of sodium hydroxide in dilute solution on glycerol in dilute solution is only $+0.22$ Cal., compared with 0.515 developed by the action of the first molecule, but even this value is higher than the corresponding thermal disturbance, $+0.04-0.11$ Cal. in the case of alcohols. The action of sodium, sodium oxide, or sodium hydroxide on glycerol develops $+14$ Cal. more than the corresponding reaction with monosodium glyceroxide. The thermal disturbances resulting from the action of sodium, sodium oxide, and sodium hydroxide on monosodium glyceroxide are in each case about 2.0 Cal. lower than for the corresponding reaction with ethyl alcohol, a result which explains why, when two atoms of sodium act on a mixture of ethyl alcohol and glycerol, one atom is substituted in each compound, the bibasic glyceroxide only being formed at a high temperature.

C. H. B.

Freezing Mixture. By I. A. BACHMAN (*Amer. Chem. J.*, **10**, 45—47).—The spent acids (mixture of equal volumes of strong nitric and sulphuric acids) from Grove's battery, mixed with snow or broken ice till it forms a thin paste, gives a temperature of -30° .

H. B.

Relative Densities of Hydrogen and Oxygen. By LORD RAYLEIGH (*Proc. Roy. Soc.*, **43**, 356—363).—Regnault's method was adopted, but the globe was not cooled by ice, being simply inclosed during weighing in a wooden case, and the average temperature taken. The hydrogen was evolved from amalgamated zinc and platinum in sulphuric acid in a vacuum, the hydrogen being liberated by connecting the zinc and platinum plates, the gas was purified by potash and mercuric chloride, and dried with phosphoric anhydride. The oxygen was obtained from potassium and sodium chlorates. An important correction, overlooked by Regnault, is made in observing the compression which the globe suffers when exhausted; this the author determines by experiment, and from the theory of elastic shells. The ratio found is 15.884 (Regnault, 15.964), the difference being mainly due to the above correction. With Scott's ratio of atomic volumes 1.9965 (Abstr., 1888, 411), the value 15.912 is obtained for the ratio of atomic weights.

H. K. T.

Hydrate of Hydrogen Sulphide. By DE FORCRAND and VILLARD (*Compt. rend.*, **106**, 849—851).—The vapour-tension of the hydrate of hydrogen sulphide was determined in presence of excess of water and gas. The following table gives the differences between the tensions and 760 mm. at different temperature:—

0°	0.1°	0.6°	0.8°	0.85°	1.0°	1.2°	1.75°	2.1°
−29 mm.	−17	+20	+45	+48	+60	+70	+117	+147
2.8°	3.4°	3.8°	3.9°	4.5°	4.9°	5.2°		
+222	+288	+323	+337	+403	+463	+490.		

The low tension at 0° is especially noteworthy; at lower temperatures the presence of ice interferes with the determinations. The tension is, however, always below that of the atmosphere.

C. H. B.

Hydrates of Gases. By DE FORCRAND and VILLARD (*Compt. rend.*, **106**, 939—941).—According to Wroblewski, the formation of a hydrate of a gas by compression only takes place when the water holds in solution a quantity of gas corresponding with that required to produce the hydrate. It may also be supposed that at the moment of crystallisation the water contains much less gas than the hydrate, but the formation of the latter takes place with absorption of a considerable quantity of gas. The solution of a gas, and the formation of a hydrate, would then be two perfectly distinct phenomena. The second explanation only is admissible in the case of hydrates of chlorine and sulphurous anhydride, since the solutions contain a much lower proportion of these gases than the hydrates.

The apparatus used for determining the vapour-tension of the hydrate of hydrogen sulphide (preceding Abstract) was arranged so that at a pressure of 60 mm. above atmospheric pressure, it contained crystals of the hydrate, together with hydrogen sulphide and a slight excess of water. If the pressure was increased by 100 mm., and the apparatus agitated to promote the formation of more crystals, there was a considerable absorption of gas, and the pressure sank to its former value. A further increase of pressure produced a further quantity of crystals. An increase of pressure of 100 mm. does not greatly increase the solubility of the gas at constant temperature, and yet the production of the hydrate was evident from the separation of fresh crystals. When the hydrate is formed at 0°, 1 c.c. of water absorbs about 100 c.c. of gas, whereas water at +1° dissolves only 4 vols. of the gas under normal pressure. The composition of the hydrate $\text{SH}_2 + 12\text{H}_2\text{O}$ corresponds with 102 vols. of gas. Similar results were obtained with methyl chloride, and it would seem therefore that the formation of a hydrate of gas is not merely the solidification of a saturated solution, but an independent act of combination.

C. H. B.

Method for Obtaining Definite Hydrates. By E. J. MAUMENÉ and C. LIMB (*Bull. Soc. Chim.*, **48**, 777).—Crystals of oxalic acid were kept under a glass shade by the side of dried oxalic acid. After six months the crystals were titrated, and found to have a com-

position corresponding with the formula $C_2H_2O_4 + 2H_2O$. Crystals from the same preparation were kept in a desiccator over sulphuric acid for more than six months, when they had the composition indicated by the formula $C_2H_2O_4$. It is suggested that instead of drying substances indifferently over lime or sulphuric acid, some special substance should be selected, according to the nature of the compound to be analysed.

N. H. M.

Solubility of Sulphates. By A. ÉTARD (*Compt. rend.*, **106**, 740—743).—The author's determinations, extending through a wide range of temperature, show that when the solubility of a salt is represented by a curve which expresses the weight of salt in 100 parts of solution, this curve is a right line, the angular coefficient of which varies with each salt. For one and the same salt, the coefficient changes in value at one or more points, the change being usually abrupt, although in some cases the perturbation extends through a short but measurable distance. In the majority of cases, if not in all, the sign of the coefficient changes, and the solubility decreases beyond a certain temperature. This is especially marked in the case of many sulphates, and the following coefficients have been determined by the author.

Ferrous Sulphate.—From -2° to 65° , $y = 13.5 + 0.3784t$; from 65° to 98° the curve of solubility is parallel with the axis of temperature; from 98° to 156° , $y = 37.5 - 0.6685t$. The last equation indicates that the salt should be insoluble at 156° , and this conclusion has been verified experimentally.

Cadmium Sulphate.—From 0° to 68° , $y = 35.7 + 0.2160t$; from 68° to 200° , $y = 50.6 - 0.3681t$. At 200° the salt dissolves only to the extent of 2 per cent., and at 215° it is insoluble.

Magnesium Sulphate.—From 0° to 123° , $y = 20.5 + 0.2276t$; from 123° to 190° , $y = 48.5 - 0.4403t$. The salt should become insoluble at 233° , but this was not verified. A solution saturated at $+15^\circ$ becomes turbid at 178° , and deposits a hydrate in porcelain-like crusts.

Lithium Sulphate.—From -20° to -10.5° , $y = 18.5 + 0.8421t$; from -10.5° to 100° , $y = 26.5 - 0.0274t$.

Rubidium Sulphate.—From 0° to 49° , $y = 26.5 + 0.2959t$; from 49° to 170° , $y = 41.0 + 0.0661t$.

Potassium Selenate.—From -20° to 100° , $y = 52 + 0.0250t$.

Selenious Anhydride.—From -3° to 36° , $y = 45.0 + 0.7692t$.

In several cases the observations are complete, since they extend from the point of congelation of the solution to the temperature at which the salt again becomes insoluble. The point of congelation corresponds with a certain ratio between the salt and the water. As the temperature rises, the change in presence of an excess by the salt is analogous to etherification. A certain quantity of water is set free, and dissolves a further quantity of the salt, and this change continues as the temperature rises, the solubility of the salt increasing by reason of the dehydration of the original system up to the point of maximum solubility. A change analogous to saponification then sets in, and as the temperature rises the salt is gradually

deposited, the water playing an increasing part in the establishment of equilibrium until at a certain temperature the water completely displaces the salt, and the latter becomes insoluble. C. H. B.

Laws of Chemical Equilibrium. By P. DUHEM (*Compt. rend.*, 106, 846—849).—A continuation of the discussion with Le Chatelier. C. H. B.

Raoult's Method for the Determination of Molecular Weight and on Acetoxime. By K. AUWERS and V. MEYER (*Ber.*, 21, 1068—1070).—The authors suggest that in Raoult's method glacial acetic acid should always be employed as the solvent, and neither benzene nor water.

Beckmann's determinations of the molecular weight of oximes (this vol., p. 409) are probably wrong, owing to his having used benzene. Experiments made by the authors on acetoxime show that when glacial acetic acid is used, the results obtained agree with the formula C_3H_7NO .

When it is absolutely necessary to make use of water or benzene, the results are of value only after having first made experiments with a compound of strictly analogous constitution, the molecular weight of which is known. F. S. K.

Molecular Weight of Oximes. By E. BECKMANN (*Ber.*, 21, 1163—1164).—The conclusions arrived at by the author with reference to the molecular weights of the oximes (this vol., p. 409) were based on the lowering of the freezing point of benzene, which was employed as the solvent for the various oximes examined. When, however, acetic acid is used, results are obtained which, in the case of acetoxime and benzaldoxime, are in agreement with the molecular weights usually adopted. The molecular weights of these oximes as determined by the lowering of the vapour-tension of their ethereal solutions are also those ordinarily assumed. W. P. W.

Apparatus for Fractional Distillation. By E. CLANDON and E. C. MORIN (*Bull. Soc. Chim.*, 48, 804—811).—The apparatus is intended for the distillation of large amounts of liquids, 100 litres for example. It is made entirely of copper. For description of the apparatus the original paper, in which sketches are given, must be referred to. N. H. M.

Apparatus for Fractional Distillation. By T. H. NORTON and A. H. OTTEN (*Amer. Chem. J.*, 10, 62—69).—The apparatus is constructed on the principle of Tcherniac's "déverseur" for the separation of froth during distillation (*Wurtz Dict.*, Supp., 597), so that the vapours are not washed through the condensed liquid, but are at once separated. The apparatus is decidedly fragile, and on the whole yields no better results than the fractionating tubes of Linnemann and Hempel. H. B.

Pressure Tubes. By H. N. WARREN (*Chem. News*, 57, 155).—The author adopts the following plan to make glass tubes resist internal pressure at high temperatures. For temperatures ranging from 200° to 400°, the sealed tube is enclosed in a copper tube, the

intervening space being closely packed with magnesia. For higher temperatures, a wrought-iron external tube is used with sand as the packing material. D. A. L.

Turbine for Laboratory Purposes. By H. RABE (*Ber.*, **21**, 1200—1201).—The author has devised a simple form of turbine which, when connected with the water service of a laboratory, is capable of providing the motive power required for mechanical stirring.

W. P. W.

Lecture Apparatus for making Sulphuric Anhydride. By W. R. HODGKINSON and F. K. LOWNDES (*Chem. News*, **57**, 193).—The apparatus consists of an inverted bell-jar. The smaller opening is fitted with a caoutchouc stopper carrying a wooden rod to which a piece of stout platinum wire is attached supporting some spongy platinum in the centre of the jar. The large opening is firmly closed by a piece of wood, through which two tubes (one for oxygen, the other for sulphurous anhydride) pass and terminate close to the platinum sponge which just previous to use has been heated in a bunsen flame. Sulphuric acid forms rapidly when the two gases are made to impinge on the hot spongy platinum. D. A. L.

Inorganic Chemistry.

Relative Values of the Atomic Weights of Hydrogen and Oxygen. By J. P. COOKE and T. W. RICHARDS (*Amer. Chem J.*, **10**, 81—110; comp. Lord Rayleigh, this vol., p. 643).—The only direct determinations of this ratio that are independent of all other considerations and determinations are those of Dumas and of Erdmann and Marchand, and both these contain possible errors and uncertainties that are so great as to render the results obtained worthless for deciding between the numbers 15.96 and 16.00 as the atomic weight of oxygen.

The principal source of possible error is that the amount of hydrogen is determined by the difference of the weights of water and of oxygen, and the combined errors of these two determinations are then exaggerated because of the comparative smallness of the number that expresses the hydrogen. In the present determination the hydrogen was actually weighed. The globe used was counterbalanced by a similar one, and its weight could be satisfactorily determined to one-tenth of a milligram; it held nearly 5 litres, and was provided with glass stopcocks. After exhausting to 1 mm. it was weighed, filled with hydrogen, and again weighed.

In the first series of experiments, the hydrogen was prepared from almost pure zinc and hydrochloric acid; the dissolved air was removed from the dilute acid by boiling in a stream of hydrogen and preserving it in an atmosphere of hydrogen. The gas was purified by passing through a 5-foot tube of potash solution (necessary

to remove sulphur dioxide), then dried by calcium chloride, sulphuric acid, and phosphorus pentoxide; wherever possible, joints were made by sealing together the glass tubes, all others were protected by a cement composed of equal parts of pitch and gutta-percha. In the second series of experiments, the hydrogen was prepared from hydrochloric acid and a semi-fluid amalgam of zinc; the amalgam could be connected externally with a platinum plate immersed in the acid, and by making connection and interposing a varied electrical resistance, or by connecting with a battery, the hydrogen could be obtained at any desired speed. The gas was purified as before. In the third series, the hydrogen was prepared by dissolving sheet aluminium in pure aqueous potash. The long potash washing tube was dispensed with, but the gas dried as before. The globe was then connected with the rest of the apparatus that had previously been filled with nitrogen. The apparatus consisted firstly of heated tubes containing copper to remove oxygen from the air current, copper oxide to remove hydrogen occluded by the copper or organic matter in the air; secondly, drying tubes containing potash, calcium chloride, sulphuric acid, and phosphorus pentoxide; thirdly, the weighed globe containing hydrogen; fourthly, tube containing heated copper oxide; fifthly, the apparatus for collecting the water, namely, an empty tube, strong sulphuric acid, and phosphorus pentoxide; and, lastly, an apparatus for regulating the suction of air through the whole apparatus. The gas current was rapid the whole time; after the first half hour, more than nine-tenths of the hydrogen was burnt, and after the first hour the first tube containing copper was removed, all possibility of an explosion being at an end, and air instead of nitrogen was drawn through the apparatus. By this means the whole apparatus is left in its initial condition, namely, the reduced copper oxide is reoxidised completely, thus avoiding all error due to occlusion of hydrogen, and the condensing tubes are left also full of ordinary air. The actual experiment lasted altogether about eight hours, which time was shown to be amply sufficient. The weight of hydrogen burnt averaged 0.42 gram. The results obtained are—

	Maximum.	Minimum.	Average.	Error.
First series (5)....	15.977	15.937	15.954	± 0.0048
Second series (5)..	15.962	15.942	15.953	± 0.0022
Third series (6) ..	15.967	15.937	15.952	± 0.0035
Average of the three series			15.953	± 0.0017
Dumas obtained			15.960	± 0.0070

or, having regard only to the substances actually weighed, the composition of water is:—Oxygen (Dumas) 88.864 ± 0.0044 , and hydrogen (Cooke and Richards) 11.140 ± 0.0011 ; total 100.004.

The results recently given by Keiser (Abstr., 1887, 1078) namely, 15.873, 15.897, and 15.826 are not concordant, and are vitiated by varying impurities in the gas used.

H. B.

Atomic Weight of Oxygen. By E. W. MORLEY (*Amer. Chem. J.*, **10**, 21—26).—It is pointed out that the conclusion drawn by Scott (this vol., p. 411) as to the ratio in which hydrogen and oxygen combine is not warranted by his experimental method, more particularly because the amount of impurities in the hydrogen and in the oxygen used were not separately estimated. Methods are proposed by which these impurities can be estimated and allowed for, and also new methods for effecting the synthesis of water in the most exact manner. H. B.

Oxidation of Solutions of Sulphurous Anhydride and Sulphites. By I. A. BACHMAN (*Amer. Chem. J.*, **10**, 40—41).—Solutions of normal potassium, sodium, and ammonium sulphites were completely oxidised in three weeks, whilst sulphurous acid had lost by volatilisation and oxidation three quarters of its strength, and acid ammonium sulphite had only lost about 45 per cent. All the solutions contained 10 grams of sulphurous anhydride per litre, were kept in open bottles, and shaken twice daily. H. B.

Sulphites. By A. RÖHRIG (*J. pr. Chem.* [2], **37**, 217—253).—The author has revised the work of Muspratt (*Annalen*, **50**, 259), Rammelsberg (*Ann. Phys. Chem.*, **67**, 245), and others, and has fully described the sulphites of lithium, thallium, the alkaline earths, lead, magnesium, zinc, cadmium, aluminium, uranium, bismuth, iron, chromium, manganese, nickel, cobalt, and tin, with the result, in general, that the older observations are confirmed. Attempts to obtain the two isomeric salts NaSO_2OK and KSO_2ONa were not successful, only one potassium sodium sulphite being formed under any circumstances. G. T. M.

Simple Formation of Thiosulphates. By E. DONATH and F. MÜLLNER (*Dingl. polyt. J.*, **267**, 143).—This method is based on the oxidation of metallic sulphides in aqueous solution by boiling with manganese dioxide. D. B.

New Sulphur Oxy-acid. By A. VILLIERS (*Compt. rend.*, **106**, 851—853).—Sodium thiosulphate is mixed with a quantity of water insufficient for complete solution, and the mixture is saturated with sulphurous anhydride. If any salt now remains undissolved more water is added, and the mixture is again saturated with the gas. A yellow solution is obtained, and if this is evaporated immediately in a vacuum, it evolves sulphurous anhydride, and, if the temperature does not exceed 0° , only sodium thiosulphate is obtained from the residue. If the solution is allowed to remain at the ordinary temperature for two or three days, it will then absorb more sulphurous anhydride, and if after saturation it is allowed to remain for a day or two and is then evaporated in a vacuum over sulphuric acid, it yields brilliant, white, brittle, anhydrous prisms of the composition $\text{Na}_2\text{S}_4\text{O}_6$. When these crystals are dissolved in water and evaporated as before, the hydrate $\text{Na}_2\text{S}_4\text{O}_6 + 2\text{H}_2\text{O}$ is obtained in soft, waxy crystals arranged in nodules.

If the mother-liquor from the first crystals is concentrated, it yields small crystals of the trithionate $\text{Na}_2\text{S}_3\text{O}_6 + 3\text{H}_2\text{O}$, which has not previously been crystallised. The formation of these salts is represented by the following equations:— $2\text{Na}_2\text{S}_2\text{O}_3 + 5\text{SO}_2 = 2\text{Na}_2\text{S}_4\text{O}_8 + \text{S}$ and $2\text{Na}_2\text{S}_2\text{O}_3 + 3\text{SO}_2 = 2\text{Na}_2\text{S}_3\text{O}_6 + \text{S}$. At a low temperature very little sulphur is actually liberated, and it seems to unite with the thiosulphate, forming a salt of the composition $\text{Na}_2\text{S}_3\text{O}_3$.

The salt $\text{Na}_2\text{S}_4\text{O}_8$ may be regarded as a derivative of dithiopersulphuric acid, $\text{H}_2\text{O}, \text{S}_2\text{O}_7, \text{S}_2$.
C. H. B.

Formation of Crystallised Selenates in the Dry Way. By L. MICHEL (*Compt. rend.*, **106**, 878—881).—The selenates described were prepared by fusing the chloride of the particular metal with an alkaline selenate and some sodium chloride, cooling very slowly, and extracting with water. The insoluble residue is a mixture of crystals with a crystalline powder, and if the latter is mixed with sodium chloride and heated until the greater part of the solvent is volatilised, crystals several millimetres in length are obtained.

Barium selenate forms colourless or bluish-white crystals with a vitreous lustre; hardness 3 to 4; sp. gr. 4.75. They are rhombic octahedra elongated along the greater diagonal, and are frequently arranged in groups parallel with h' . In form and optical property, they are identical with barytes.

Strontium selenate forms rhombic prisms of sp. gr. 4.23, closely resembling the crystals of celestine from Lake Érie, and precisely similar to celestine in crystallographic and optical properties.

Calcium selenate forms colourless or milk-white rectangular lamellæ of sp. gr. 2.93; hardness 3.5. It melts before the blowpipe without exfoliation, and is only slightly soluble in water or nitric acid. Hydrochloric acid attacks it slowly with evolution of chlorine. Optical examination shows that its properties are very similar to those of anhydrite.

Lead selenate cannot be obtained in the same way, but a mixture of the amorphous selenate, lead nitrate, and sodium nitrate yields small rhombic prisms with all the characters of anglesite.

Measurements of the angles of the crystals, &c., are given in the paper. From the results it follows that the artificially prepared anhydrous selenates of barium, calcium, strontium, and lead, are isomorphous with one another and with the corresponding natural sulphates.
C. H. B.

Arsenic Nitride. By I. A. BACHMAN (*Amer. Chem. J.*, **10**, 42—44).—When a tube containing silver cyanide and arsenious oxide is heated at 300—400°, a dark-brown substance is formed as a coating over the arsenious oxide crystals. The mixture contains about 2 per cent. of nitrogen with only a trace of carbon, and is probably the hitherto unknown arsenic nitride.
H. B.

Decomposition of Ammonium Chloride by Phosphoric Acid. By K. W. JURISCH (*Dingl. polyt. J.*, **267**, 424—431).—The author has investigated Witt's process (*Ger. Pat.* 34395, May, 1885) for the

preparation of hydrochloric acid, and ammonia from ammonium chloride by decomposition with phosphoric acid. The method is intended to replace the troublesome distillation of the mother-liquors by means of lime, and to recover the chlorine lost in the calcium chloride. The separation of the ammonium chloride is effected either by evaporation to dryness and sublimation, or by fractional crystallisation. The author found that of 12 mols. of phosphoric acid employed, 8 mols. are taken up and 4 mols. remain as free acid, half being orthophosphoric acid, the remainder pyrophosphoric acid. In order to complete the decomposition at a low temperature without volatilising the ammonium chloride, an excess of phosphoric acid is required, hydrochloric acid only being expelled. On subsequently increasing the temperature, from 63 to 86 per cent. of ammonia is given off. The residue which consists of metaphosphoric acid with some ammonium metaphosphate may be used for the decomposition of a fresh portion of ammonium chloride, so that it is possible to decompose ammonium chloride in succession by the same quantity of phosphoric acid without loss of acid. Owing to the difficulty of obtaining a material for lining the furnace or other vessel capable of resisting the action of fused phosphoric acid, the application of the process on a large scale has hitherto been impossible. According to Brunner, Mond, and Co., even platinum is so energetically attacked by the acid that it cannot be employed for the heating vessel.

D. B.

Oxidation of Silver. By H. LE CHATELIER (*Bull. Soc. Chim.*, **48**, 342—345).—When pure precipitated silver is heated in oxygen at 300° under a pressure of 15 atmospheres it is slowly oxidised. The oxidation could not be completed, and the largest amount of silver oxidised was 50 per cent. The decomposition of silver oxide at the same temperature was found to be extremely slow; the pressure increased for three days, and then remained constant at about 10 atmospheres. The tension at which the oxide decomposes at 300°, is, therefore, between 10 and 15 atmospheres. At 400—450° silver oxide decomposes rapidly.

N. H. M.

Alloys of Calcium and Zinc. By T. H. NORTON and E. TWITCHELL (*Amer. Chem. J.*, **10**, 70—72).—Following the directions of Caron (*Compt. rend.*, **50**, 547) calcium chloride, zinc and sodium were heated together, but the alloys obtained did not contain more than 2·3 to 6·4 per cent. of calcium, instead of 10 to 15 per cent. as reported. The poorest alloy melted at 360°, the same temperature as zinc, but it is remarkable that the richer alloys melted at as high a temperature as 640°. They do not decompose water, or oxidise at ordinary temperatures in the air, and the zinc cannot be removed by volatilisation in a current of hydrogen without losing considerable quantities of calcium.

H. B.

Action of Metallic Oxides on Solutions of Zinc and Manganese Chlorides. By G. ANDRÉ (*Compt. rend.*, **106**, 854—856).—The finely divided oxides were heated or boiled with water and zinc

chloride until they were completely dissolved, or until no further change was observed, and the solutions were slowly cooled.

Zinc chloride and yellow mercuric oxide yield the white, amorphous zinc oxychloride, $2\text{ZnCl}_2, 3\text{ZnO} + 11\text{H}_2\text{O}$, which when washed with alcohol and dried on paper, changes to $\text{ZnCl}_2, 4\text{ZnO} + 6\text{H}_2\text{O}$. It is remarkable that mercuric oxide yields only a zinc oxychloride, since with magnesium chloride it forms a double oxychloride (Abstr., 1887, 446 and 447).

Lead oxide and zinc chloride yield brilliant, white, slender needles, which contain an almost constant proportion of chlorine, whilst the proportions of lead and zinc vary. In most cases, they are a compound of $\text{ZnCl}_2, 3\text{ZnO}$ with $\text{ZnCl}_2, \text{PbO}$. The latter compound may be regarded as lead oxychloride in which the zinc lead chloride has been replaced by the zinc salt.

Cupric oxide and zinc chloride yield a green powder of the composition $\text{Zn}_3\text{Cu}_3\text{Cl}_4\text{O}_6 + 6\text{H}_2\text{O}$, or supposing it to be derived from the well-known oxychloride, $\text{ZnCl}_2, 3\text{ZnO}$, it may have the constitution $(\text{ZnCl}_2, \text{ZnO}, 2\text{CuO})(\text{ZnCl}_2, 3\text{CuO}) + 6\text{H}_2\text{O}$. Cupric oxide and manganese chloride produce an apple-green powder, $\text{MnCl}_2, 3\text{CuO} + 3\text{H}_2\text{O}$, which may be regarded as the unknown oxychloride, $\text{MnCl}_2, 3\text{MnO}$, in which cupric oxide has replaced manganous oxide. It is not affected by boiling with a solution of manganous chloride.

Lead oxide and manganese chloride yield lead chloride only, but if the mother-liquor is poured into cold water, the compound $2\text{PbCl}_2, 2\text{PbO} + 3\text{H}_2\text{O}$, is obtained as a flocculent precipitate.

Attempts to obtain ammoniacal oxychlorides in which the base of the oxide was different from the base of the chloride were unsuccessful.

C. H. B.

Supposed Dissociation of Zinc Oxide: Condition of the Atmosphere within a Platinum Vessel heated by a Gas Flame.
By H. N. MORSE and W. M. BURTON (*Amer. Chem. J.*, 10, 148—153).
—When zinc oxide is heated for many hours in platinum vessels in a muffle furnace to a temperature above the melting point of steel, it does not lose weight, nor is the crucible in any way altered; but when heated over a gas-lamp or blowpipe there is a constant loss of weight, as has been noticed by Erdmann and by Marignac, who ascribed the loss to dissociation of the oxide. The explanation is, however, disproved by the above stated behaviour of zinc oxide in a muffle furnace, and by the fact that the atmosphere within a platinum vessel strongly heated by a gas flame always contains free hydrogen, which reduces the zinc oxide. The hydrogen is produced by the dissociation of the water produced in the cooler parts of the flame, and is then occluded by the platinum, and so passes through the crucible. A platinum tube connected with a gas burette, the whole holding 130 c.c. of air, was heated with a blast-lamp for 1, 2, 3, and 4 hours, when 54, 88.5, 98.1, and 100 per cent. of the oxygen of the confined air disappeared, and in the last two cases, moreover, 2.4 and 2.7 c.c. of free hydrogen were present, so that at least 22.8, 44, 44.5, and 48.2 c.c. of hydrogen must have passed through the platinum. This amount is increased from 22.8 c.c. to

28.5 c.c. by slightly diminishing the internal pressure by 30 mm., and is decreased to 20.9 by increasing the pressure by the same amount. Similar results were obtained by using an ordinary bunsen burner. In all cases only the outer or oxidising flame was allowed to touch the tube. The bearing of these facts on the ignition of precipitates in platinum vessels is obvious.

H. B.

Colloidal Cadmium Sulphide. By E. PROST (*Chem. Centr.*, 1888, 32, from *Bull. Acad. Belg.* [3], 14).—Colloidal cadmium sulphide can be prepared by completely precipitating an ammoniacal solution of cadmium sulphate with hydrogen sulphide, washing the sulphide with water by decantation, suspending the precipitate in water, and submitting it to a slow stream of hydrogen sulphide, the precipitate becomes first flocculent, then milky, and finally disappears entirely. The solution is then boiled until lead paper shows the absence of hydrogen sulphide. The solution is a beautiful golden-yellow by transmitted and fluorescent by reflected light. The composition of the dissolved substance is CdS . Dilute solutions remain unchanged for a long time. A solution containing 4 grams of sulphide to the litre remained clear many days, but another solution containing 11 grams to the litre coagulated in 24 hours. The following are the results of experiments on the coagulation of the colloidal sulphide.

(1.) There is no relation between the molecular weight of acid and salt and their coagulating activity. (2.) The coagulating power of salts is determined by the metal they contain. The greater the valency of the metal they contain, the greater their energy. The influence of the acid is generally not marked. Potassium sulphate coagulates in dilutions of 1 in 1666 parts, aluminium sulphate in dilutions of 1 in 232,558 parts. (3.) Among the alums, those of the triad metals are most active. (4.) The coagulating power of acid salts appears to be greater than that of normal salts. (5.) Cadmium salts are very active in coagulating the sulphide, 1 part in 250,000 of cadmium sulphate and 1 part in 285,714 of cadmium nitrate sufficing.

Most of these results agree with Schulze's results with arsenic and antimony sulphides. The concentration of the colloidal sulphide is without influence on the manner in which it coagulates.

J. P. L.

Action of Heat on Oxides and Salts of Manganese. By A. GORGEU (*Compt. rend.*, 106, 743—746).—Anhydrous manganous oxide heated rapidly and strongly yields the red oxide, but if care is taken to avoid incandescence, and the oxide is heated to dull redness until its weight is constant, the sesquioxide is obtained. The oxidation at 200° to 430° of the manganous oxide prepared at a high temperature ceases with the formation of the oxide $\text{MnO}_2, 4\text{MnO}$, but if the manganous oxide was prepared at a dull red heat and is oxidised for the same time below 430° it yields a higher oxide, which, however, contains less oxygen than the sesquioxide. The action of air at 200 — 430° on manganous oxide prepared below 400° could not

be determined directly, because the oxide is pyrophoric either at the ordinary temperature or at 140° , but the conclusion just stated was deduced from the behaviour of the carbonate and oxalate.

The red oxide, even if prepared at a red heat, will oxidise in the air after being finely powdered, the oxidation taking place more rapidly and at a lower temperature the lower the temperature at which the oxide was produced. Trimanganese tetroxide prepared at a red heat never yields an oxide higher than the sesquioxide, and the time required to obtain this result is longer the higher the temperature at which the original oxide was formed. Samples of this oxide prepared at $250\text{--}300^{\circ}$ and heated at $200\text{--}430^{\circ}$ yield the oxide $3\text{MnO}_2, 2\text{MnO}$, but these are the only exceptions to the formation of the sesquioxide. The sp. gr. of the more easily oxidised varieties of trimanganese tetroxide is usually below 4.70, whilst that of the varieties which oxidise with difficulty is generally above 4.8.

In making estimations of manganese, it is advisable to heat the oxide to bright redness for a few minutes. Under these conditions, the absorption of oxygen during cooling is absolutely *nil*.

Manganese sesquioxide prepared at a dull red heat undergoes no alteration in the air at a temperature below that at which it was formed. The natural sesquioxide, $\text{Mn}_2\text{O}_3, \text{H}_2\text{O}$, however, oxidises easily at $275\text{--}295^{\circ}$, and yields the pure dioxide. It follows that the sesquioxide only oxidises in presence of air when it has been produced at a low temperature.

The oxides formed by the action of heat on manganous carbonate, oxalate, tartrate, or acetate are similar to those obtained from manganous oxide formed at the temperature at which the particular salt decomposes.

Manganous chloride, bromide, iodide, or fluoride decomposes when heated to redness in presence of moist air, and eventually yields the crystallised oxide Mn_3O_4 below a red heat. The iodide decomposes at 250° , and yields at first the oxide Mn_3O_4 , but this is converted into the sesquioxide by heating to dull redness, or into the oxide $3\text{MnO}_2, 2\text{MnO}$ below 430° . The bromide forms trimanganese tetroxide, and afterwards the sesquioxide; the fluoride forms only the sesquioxide. The chloride at a dull red heat yields crystals of the oxychloride $2\text{Mn}_2\text{O}_3, \text{MnCl}_2$.

The oxides obtained, in addition to the four well-known oxides, are $\text{MnO}_2, 4\text{MnO}$ and $3\text{MnO}_2, 2\text{MnO}$. but these are amorphous, and it is possible that they are merely mixtures and not distinct species.

C. H. B.

Action of Iodine on Iron. By G. FLEURY (*J. Pharm.* [5], 16, 529—530).—The two elements in presence of water react with evolution of a considerable amount of heat. If the temperature is kept down to about 15° , the action soon ceases, although the iodine dissolves completely and strongly colours the liquid. On filtering, the residue consists of black iron without any peroxide. A different result follows if the mixture is heated to boiling, the red coloration quickly disappears, and a notable quantity of ferric oxide is found in the residue. To dissolve all the iron, a large excess of iodine is necessary, and conversely a large excess of iron is required to convert

all the iodine into ferrous iodide. The foregoing is explained by supposing that the ferric iodide first formed is decomposed by the heat, yielding ferric oxide and hydriodic acid; the latter then acts on the free iron forming ferrous iodide. Hence the mutual action of the two elements is not so simple as is usually supposed. J. T.

Double Salts of Sesquichlorides with other Metallic Chlorides. By G. NEUMANN (*Annalen*, **244**, 328—349).—The following double salts were prepared by adding a metallic chloride to a hot, strong solution of ferric chloride in hydrochloric acid (sp. gr. 1.19): $4\text{KCl}, \text{Fe}_2\text{Cl}_6 + 2\text{H}_2\text{O}$, reddish-brown octahedra and rhombic dodecahedra; $4\text{NH}_4\text{Cl}, \text{Fe}_2\text{Cl}_6 + 2\text{H}_2\text{O}$, dark-red crystals; $4\text{RbCl}, \text{Fe}_2\text{Cl}_6 + 2\text{H}_2\text{O}$, small, yellow crystals; $2\text{MgCl}_2, \text{Fe}_2\text{Cl}_6 + 2\text{H}_2\text{O}$, large, brownish-yellow, hygroscopic crystals; $2\text{BeCl}_2, \text{Fe}_2\text{Cl}_6 + 2\text{H}_2\text{O}$, small orange crystals.

The double chromic chlorides can be prepared by adding a relatively small quantity of the chloride of an alkali to a solution of chromic chloride (dry) in 96 per cent. alcohol. The solution is saturated with hydrogen chloride and boiled; on cooling, the double salts are deposited in crystals. Those described are $4\text{KCl}, \text{Cr}_2\text{Cl}_6 + 2\text{H}_2\text{O}$; $4\text{RbCl}, \text{Cr}_2\text{Cl}_6 + 2\text{H}_2\text{O}$; $4\text{NH}_4\text{Cl}, \text{Cr}_2\text{Cl}_6 + 2\text{H}_2\text{O}$; $2\text{MgCl}_2, \text{Cr}_2\text{Cl}_6 + 2\text{H}_2\text{O}$; $2\text{BeCl}_2, \text{Cr}_2\text{Cl}_6 + 2\text{H}_2\text{O}$; $6\text{TiCl}_4, \text{Cr}_2\text{Cl}_6$.

Double aluminium chlorides could not be obtained except in one isolated experiment, which yielded beautiful crystals of the composition $4\text{KCl}, \text{Al}_2\text{Cl}_6 + 2\text{H}_2\text{O}$.

The thallic double salts are prepared by passing chlorine into a solution of thallic chloride and the alkali chloride in strong hydrochloric acid. The anhydrous salts crystallise in rhombic plates, and the hydrated salts belong to the quadratic system. The following salts were prepared:— $2\text{TiCl}_4, \text{Ti}_2\text{Cl}_6$; $6\text{TiCl}_4, \text{Ti}_2\text{Cl}_6$; $6\text{NH}_4\text{Cl}, \text{Ti}_2\text{Cl}_6$; $6\text{RbCl}, \text{Ti}_2\text{Cl}_6$; $3\text{BeCl}_2, \text{Ti}_2\text{Cl}_6$; $6\text{KCl}, \text{Ti}_2\text{Cl}_6 + 4\text{H}_2\text{O}$; $6\text{NH}_4\text{Cl}, \text{Ti}_2\text{Cl}_6 + 4\text{H}_2\text{O}$.

W. C. W.

Ammoniacal Derivatives of Nickel Salts. By G. ANDRÉ (*Compt. rend.*, **106**, 936—939).—A cold solution of nickel chloride is saturated with ammonia, gently heated until the crystalline precipitate dissolves, and allowed to cool, when it deposits transparent, violet octahedra of the composition $2(\text{NiCl}_2, 6\text{NH}_3) + \text{H}_2\text{O}$. The crystalline precipitate has the same composition, and the compound can also be obtained in large, opaque octahedra containing 3 mols. H_2O , by passing ammonia into a solution of ammonium chloride containing nickel oxide in suspension. When boiled with water, or heated in sealed tubes at 200° , the ammoniacal compound yields amorphous nickel oxide.

If a solution of nickel chloride is gradually mixed with a limited quantity of dilute ammonia and the precipitate washed with cold water and dried at 100° , it has the composition $\text{NiCl}_2, 8\text{NiO} + 13\text{H}_2\text{O}$.

When ammonia is passed for a long time into a cooled solution of nickel sulphate and the liquid gently heated, large, deliquescent, pale-violet needles of the composition $2\text{NiSO}_4, 10\text{NH}_3 + 7\text{H}_2\text{O}$ separate

on cooling. A sulphate of the usual type, $\text{NiSO}_4 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$, was described by Erdmann and Laurent.

If ammonia is passed into a solution of ammonium sulphate containing nickel oxide in suspension in the proportion of 1 mol. of oxide to 2 of the salt, and the liquid is heated and allowed to cool, large, blue, rhombic prisms of the salt $2[\text{NiSO}_4 \cdot (\text{NH}_3)_2 \cdot \text{SO}_4 \cdot 6\text{NH}_3] + 3\text{H}_2\text{O}$ are obtained. The same compound is obtained on passing ammonia into a solution of the two sulphates in equivalent proportions.

The salt $2[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3] + 3\text{H}_2\text{O}$ is obtained by passing ammonia into a solution of nickel nitrate, or into a solution of ammonium nitrate containing nickel oxide in suspension. The nitrate described by Erdmann was not obtained. Nickel, like cadmium, forms only one ammoniacal nitrate, and the two salts are analogous, but differ from the ammoniacal nitrates of copper and zinc. C. H. B.

Metallurgy of Bismuth. By E. MATTHEY (*Proc. Roy. Soc.*, **43**, 172—173).—Instead of the usual wet method, the author removes copper from bismuth by fusion with bismuth sulphide, the copper displacing the bismuth in the sulphide. By this means 90 per cent. of pure metal can be obtained from the crude material, the mixed sulphides being also suitable for reduction and resmelting. Other impurities, arsenic, antimony, lead, &c., are first removed (comp. Abstr., 1887, 900). The bismuth operated on contained 0.1—1.0 per cent. copper. H. K. T.

Separation of Platinum from Rare Metals. By H. PIRNGRUBER (*Chem. Centr.*, 1888, 84—85, from *Eng. and Min. J.*, **44**, 256).—The ores are first treated with chlorine-water to remove any gold, and then with aqua regia under pressure. Osmium and iridium and some of the rhodium and ruthenium remain undissolved. The solution is boiled with soda and treated with alcohol and potassium chloride; after acidifying with hydrochloric acid, potassium platinochloride separates, from which the platinum is obtained by reduction. The metals remaining in solution are precipitated with zinc or iron.

The insoluble residue left on treatment with aqua regia is heated in a porcelain retort in a stream of air or oxygen; osmium oxidises and volatilises as OsO_4 , which decomposes into the metal and oxygen at a red heat. The residue in the retort and the metals obtained by precipitation with zinc or iron are united and melted with four times their quantity of zinc under a covering of zinc chloride; the alloys are heated with hydrochloric acid until palladium begins to dissolve, and the solution turns brown. The black residue left after decanting off the liquid is boiled with aqua regia: part of the rhodium and ruthenium remains undissolved. From this solution, after treatment with soda, the palladium is precipitated as iodide with potassium iodide, avoiding excess; the iodide is reduced with hydrogen, the metal dissolved in concentrated nitric acid, and reprecipitated as the double salt with potassium chloride, which is again reduced with hydrogen.

The solution from which the palladium has been separated is reduced with hydrogen, when all the metals, with the exception of

iridium, are precipitated. The solution is filtered and the filtrate oxidised by boiling with aqua regia. The iridium is precipitated with potassium chloride as potassium iridiochloride in dark-red cubes; the metal is obtained by simply heating the compound.

The precipitate of metals obtained by reduction with hydrogen is mixed with the rhodium and ruthenium and treated with zinc and hydrochloric acid. The black powder is then heated with barium chloride in a stream of chlorine, any osmium that may still remain will be volatilised as OsCl_2 . The residue, a barium rhodiochloride, is dissolved in water and the barium removed with sulphuric acid. On the addition of sodium hydrogen sulphite to the filtrate, a yellow salt ($3\text{Na}_2\text{O}, \text{Rh}_2\text{O}_3, 6\text{SO}_2$) is precipitated. This salt when treated with boiling sulphuric acid and the excess of acid driven off, is converted into the double salt $\text{Na}_2\text{O}, \text{Rh}_2\text{O}_3, 4\text{SO}_3$, which is insoluble in acids and water, but is decomposed by potash, the hydroxide being formed. If this is dissolved in hydrochloric acid and reduced with hydrogen, the metal is obtained.

To obtain ruthenium, the osmium-iridium residue is melted with zinc and treated with hydrochloric acid as above. The insoluble metallic powder is then boiled with potash and potassium chromate, and subsequently heated with sodium sulphate after the addition of an excess of potash; only ruthenium is precipitated. J. P. L.

Mineralogical Chemistry.

Sellaïte. By A. SELLA (*Chem. Centr.*, 1887, 1236, from *Rend. Acc. Lincei* [4], 3, 529—530).—The author has met with sellaïte in anhydrite found in the Gébroulaz Glacier near Montiers, in Savoy. Strüver determined the form of the prismatic sellaïte crystals and found them on analysis to be composed of magnesium fluoride. Cossa also, from magnesium fluoride, prepared artificial sellaïte which corresponded with the natural product. The author now confirms the composition. Albite, fluorite (in cubo-dodecahedrons), quartz, and dolomite in beautiful tabular, transparent crystals (some forms hitherto undescribed) were found with this mineral.

Sellaïte occurs there in anhydrite which changes to gypsum, and contains sulphur and dolomite interstratified with it. J. P. L.

Proustite containing Antimony. By H. A. MIERS and G. T. PRIOR (*Min. Mag.*, 7, 196—200).—A magnificent specimen of proustite from Chañarcillio, Chili, has been recently acquired for the British Museum. It is a mass of lustrous crystals, measuring 3 inches by $2\frac{1}{2}$ inches, and 3 inches in height. The forms observed were $-\frac{1}{2}R$, $-2R$, $R3$, $-2R\frac{3}{2}$. The rhombohedron angle was found on measurement to be $72^{\circ} 12'$. On analysis the mineral was found to contain 13.85 per cent. of arsenic and 1.41 per cent. of antimony. Its

sp. gr. is 5.64. The analyses made prove that the antimony is very unevenly distributed throughout the specimen. It is probably present in smaller quantities in the better crystallised parts, and possibly the surface of the crystals contains no antimony. It is certain that in the crystals analysed the presence of more than 1 per cent. of antimony has no appreciable effect on the rhombohedral angle.

B. H. B.

Copper Antimonide. By A. LAIST and T. H. NORTON (*Amer. Chem. J.*, 10, 60—62).—This new mineral comes from near Mytilene in Eastern Asia Minor, and is found in large quantity. It is lustrous, silver-white, tarnishes easily, shows no crystalline structure, is very brittle, and has a hardness of 4 to 5. Its melting point lies between that of antimony glance and of natrolite. Its specific gravity is as high as 8.812. Analysis gives—

Cu.	Sb.	Total.
73.37	26.86	100.23

a composition lying between that required by the formulæ Cu_5Sb and Cu_6Sb , and corresponding closely with Ag_6Sb , the only known native antimonide besides Ag_3Sb . A very similar substance is obtained by fusing the ingredients in the above proportions. The mineral is termed *horsfordite*.

H. B.

Varvacite. By P. H. WALKER (*Amer. Chem. J.*, 10, 41—42).—The sample was from Austinville, Wythe Co., Va., U.S., and occurs imbedded in psilomelane and ferruginous clay in radiating fibrous crystals.

MnO_2 .	MnO .	BaO .	H_2O .	SiO_2 .	Fe_2O_3 and Al_2O_3 .
68.86	7.51	14.42	5.08	1.98	2.23 = 100.08

H. B.

Occurrence of Oxide of Cobalt. By H. RÖSSLER (*Dingl. polyt. J.*, 267, 518—520).—The ancient Saxon and Swedish ores which contain cobalt in combination with arsenic and were formerly almost exclusively used for the manufacture of cobalt, have for some time ceased to meet the increasing demand for this metal, by far the largest proportion being now extracted from the manganeseiferous brown iron ores of New Caledonia. These contain about 2 per cent. of cobalt and the same quantity of nickel. Cobalt is also present in considerable quantity in the black copper ores of the Spanish province of Leon. It occurs also in iron ores and in numerous manganese ores. Its occurrence in porphyry at Imsbach near the Donnersberg, in the Palatinate of the Rhine, is of interest, inasmuch as a fissure about one metre in width traverses the rock which is filled up with a loose mass of ferric and manganic oxides containing about 0.3 per cent. of cobalt and 0.1 per cent. of nickel, besides copper and lead. This fissure is estimated to contain at least 30,000 kilos. of cobalt.

The author, in conclusion, suggests the recovery of cobalt from iron and copper pyrites.

D. B.

Strontianite and Celestine from the Kaiserstuhl. By J. BECKENKAMP (*Zeit. Kryst. Min.*, **14**, 67—73).—Strontianite, a mineral hitherto unknown in Baden, has been found by the author at Oberschaffhausen. On analysis it gave the following results:—

CaO.	SrO.	CO ₂ .	Mg.	Fe.	Total.
4.91	63.94	30.92	trace	trace	99.77

It occurs in prismatic crystals, and in crystals resembling tetrahedra, which are shown to be hemimorphic. At the same locality, the author found blue crystals of celestine. B. H. B.

Chemical Structure of Natural Silicates. By F. W. CLARKE (*Amer. Chem. J.*, **10**, 120—128).—From the relatively small number of silicates and the repeated occurrence of the same silicates under the most varied circumstances, it follows that their constitution must be comparatively simple. They may generally be regarded as substitution derivatives of ortho- or of meta-silicic acid, or of polymerides of the same acids. To these views the author was led by noticing the change of topaz into muscovite ($\text{Al}_2\text{SiO}_4\text{F}_2$ into $\text{Al}_3\text{KH}_2(\text{SiO}_4)_3$); these formulæ exhibit no distinct relationship until the former is trebled, and both are written as orthosilicates, $\text{Al}(\text{SiO}_4\text{Al})_2\text{SiO}_4(\text{AlF}_2)_3$, and $\text{Al}(\text{SiO}_4\text{Al})_2\text{SiO}_4\text{KH}_2$. The following minerals are cited as being orthosilicates, and constitutional formulæ are assigned to them: Xenolite, fibrolite, paragonite, eucryptite, dumortierite, grossularite, prehnite, and natrolite; the formulæ exhibit relationships that are confirmed by the mode of occurrence of the several minerals. The same holds good with the alteration products westantite, montmorillonite, and kaolinite, and with the polymerides annite, sedulite, nosean, and ultramarine.

The metasilicate of aluminium does not occur native; it might be written either $\text{SiO}_3(\text{Al}\cdot\text{SiO}_3)_2$, or $\text{Al}(\text{SiO}_3)_3\text{Al}$, but as far as can be judged from the native metasilicates, the former formula is the only one admissible. Spodumene, jadeite, leucite, pyrophyllite, kyanite, are regarded as belonging to this class; the latter being represented as $\text{SiO}_3\cdot\text{Al}\cdot\text{O}\cdot\text{AlO}$.

There are also a couple of other silicic acids, $\text{H}_2\text{Si}_2\text{O}_6$, from which petalite is derived, and $\text{H}_4\text{Si}_3\text{O}_{10}$, from which only albite and orthoclase are derived. Other acids may exist, but it does not appear necessary to assume their existence.

By these formulæ, relationships can be traced between minerals derived from the different acids as is shown in the case of muscovite, garnet, tourmaline, and orthoclase, and albite, the constituent of all granites. The silicates, other than those of aluminium, present few difficulties in the consideration of their structure. It is possible that silicates exist that are partly ortho- and partly meta-compounds. Similarly, all double salts may be considered, but with some, as the double haloids, acetates, formates, &c., the case is not so clear.

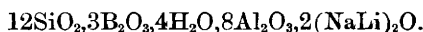
H. B.

Composition of Tourmaline. By R. B. RIGGS (*Amer. J. Sci.*, **35**, 35—51).—With the exception of the researches of Rammelsberg, very little has been done towards solving the question of the composi-

tion and constitution of the varieties of tourmaline. Rammelsberg's analyses were faulty in that the water and boric acid were not directly estimated. The direct estimation of water being possible, and a satisfactory method of determining boric acid having been devised by Gooch (Abstr, 1887, 299), new tourmaline analyses seemed desirable. The author has therefore analysed material from the following localities:—Auburn, Rumford, and Paris, in Maine; Calhao in Brazil; Dekalb, Gouverneur, and Pierrepont in New York; Hamburg in New Jersey; Orford in New Hampshire; Monroe and Haddam in Connecticut; Stony Point in North Carolina; and Nantic Gulf in Baffin's Land. These represent well the variations in physical properties and chemical composition, which characterise the different varieties of tourmaline. From the analytical results, it is evident that there are three types, lithia, iron, and magnesia tourmaline respectively, with an indefinite number of intermediate products. These types graduate from one into the other, beginning with the lithia tourmaline, and passing through the iron varieties to those of the purer magnesian type.

The following formulæ may be taken as representing typical compounds of the three varieties:—

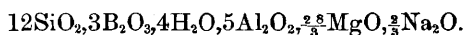
I. Lithia tourmaline—



II. Iron tourmaline—



III. Magnesia tourmaline—



The calculated theoretical composition of these types is as follows:—

	B ₂ O ₃ .	SiO ₂ .	Al ₂ O ₃ .	FeO.	MgO.	Li ₂ O.	Na ₂ O.	H ₂ O.	Total.
I.	11·00	37·70	42·75	—	—	1·57	3·21	3·77	100·00
II.	10·18	34·89	34·59	13·95	—	—	2·90	3·49	100·00
III.	10·90	37·38	26·49	—	19·31	—	2·18	3·74	100·00

On comparing these results with those of analysis, they will be found to agree closely. The boric acid found invariably falls short of the theory. This is not to be wondered at, as the analyses are made of material more or less impure, and the case would be exceptional where the impurity tended to raise the percentage of boric acid. The author intends to discuss more fully the composition of tourmaline in a paper which is to appear in a forthcoming bulletin of the United States Geological Survey.

B. H. B.

Genthite. By P. H. WALKER (*Amer. Chem. J.*, 10, 44).—A fresh analysis of a sample from Webster, Jackson Co., N.C., U.S. (Compare Dunnington, this Journal, 1872, 680). Hardness 2·5; sp. gr. 2·53.

SiO ₂ .	NiO.	MgO.	H ₂ O at 100°.	H ₂ O above 100°.	Fe ₂ O ₃ .
55·38	17·84	15·62	5·18	5·59	0·56 = 100·17

H. B.

Nickeliferous Talc. By I. A. BACHMAN (*Amer. Chem. J.*, **10**, 45).—The specimen was from Webster, Jackson Co., N.C., U.S. It is notable for the large amount of nickel contained in it:—

SiO ₂ .	NiO.	MgO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	H ₂ O at 100°.	H ₂ O above 100°.
53.91	15.91	19.39	1.46	2.65	0.80	5.50 = 99.62

H. B.

Tscheffkinit. By R. C. PRICE (*Amer. Chem. J.*, **10**, 38—39).—The specimen, a large, single block, lying loose on the ground, is from Hat Creek, Massie's Mills, Nelson Co., Va., U.S.

SiO ₂ .	TiO ₂ .	ZrO ₂ .	Ce ₂ O ₃ .	Di ₂ O ₃ .	La ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	BeO.
23.28	21.16	2.29	11.89	15.38	4.96	5.63	5.56	2.15

CaO.	MgO.	Na ₂ O.	H ₂ O.
5.48	0.64	0.32	1.90 = 100.64

Previous published analyses and also the present one approximate to the formula $2(\text{Ca, Be, Fe, Mg})\text{O}, (\text{Ce, Di, La, Fe})_2\text{O}_3, 5(\text{Si, Ti})\text{O}_2$.

H. B.

Zobtenite. By J. ROTH (*Chem. Centr.*, 1887, 1235, from *Preus. Akad. Wiss. Nat. M.*, 265—284).—Zobtenite is described as a petrographic rock belonging geologically to the crystalline schists, and corresponding to eruptive gabbro. The usual coarse-grained zobtenite is composed of saussuritic labradorite, grey or green diallage, some magnetic iron, and pyrites. The labradorite is mostly changed into an aggregate of zoisite and epidote with hornblende; the diallage into uralite. Serpentine and plagioclase-amphibolite occur in intimate association with the occasionally coarse-veined zobtenite. The same group of rocks is met with in the Baumgarten-Groschauer mountain, and the same interlacing of serpentine, hornblende schists, and zobtenite (veined gabbro) occurs also in Saxon granulite. This interlacing is seen very well at Rosswein, Böhrigen and Höllmühle. Zobtenite here and there contains hypersthene and olivine. It is also found with chloritic schists and serpentine at Wagaleite in the Fichtelgebirge, and here is composed of saussuritic labradorite with coarse grossularite, diallage, and titanite. At Frankenstein, fine and coarse-grained zobtenite is found bearing hornblende, quartz, apatite, magnetite, iron pyrites, and more rarely rhombic pyroxene and secondary biotite. The widely distributed veined zobtenite found in the Jotunfjelds of Norway, is composed of plagioclase, sea-green diallage, hypersthene, green hornblende, apatite, magnetite, spinelle, and garnet, with transitions in the schists.

The bright coloured labradorite rock of Nārödal is composed of labradorite, diallage, and garnet. The hyperytes of Vermland (plagioclase, augite, hypersthene, olivine, apatite, and titanite iron) change into dioritic rocks, and are intimately mixed with the surrounding magnetite gneiss. The modifications contain labradorite, green diallage with uralite, hypersthene, and garnet. In Roslagen, transitions of pure diorite through dioritic diallage to gabbro are found. The latter contains anorthite, diallage, hornblende, magnetite, olivine, augite, hypersthene, enstatite, apatite, mica, quartz, pyrites,

graphite, epidote, saussurite, and small quantities of zircon and picotite.

The gabbro of Radmansö is developed as gabbro, olivine-gabbro, and hornblende-gabbro, besides transitions occur as quartz, and biotite gabbro, and diallage gneiss. J. P. L.

Meteoric Iron from Nejed, Central Arabia. By L. FLETCHER (*Min. Mag.*, 7, 179—183).—A meteoric iron, weighing 59·4 kilograms, was seen to fall in the district of Nejed, Central Arabia, on June 18th, 1863. The mass is tetrahedral in shape, its length being 41 cm., and its breadth and thickness both 28 cm. The surface is covered with pittings, and there is no evidence of weathering. Analysis gave the following results:—

Fe.	Ni.	Co.	P.	Insol. residue.	Total.	Sp. gr.
91·04	7·40	0·66	0·10	0·59	99·79	7·863

Traces of copper and sulphur were observed. The black residue insoluble in aqua regia, consists chiefly of amorphous carbon containing a trace of chromite. In composition, the Nejed iron is very similar to the Trenton, Toluca, and the Verkhne Udinsk irons.

B. H. B.

Meteoric Iron from Greenbrier Co., West Virginia. By L. FLETCHER (*Min. Mag.*, 7, 183—186).—A single fragment of iron, weighing 11 lbs., was found in 1880 on the Alleghany Mountain, Greenbrier Co., West Virginia. Two pieces, weighing 63 and 31 oz. respectively, were acquired for the British Museum. Analysis gave the following results:—

Fe.	Ni.	Co.	P.	Residue.	Total.	Sp. gr.
91·59	7·11	0·60	0·08	0·12	99·50	7·869

The insoluble residue consisted of graphitic carbon, and a fine powder, small fragments, a thin elongated plate, and a single opaque black crystal with bright faces and a metallic lustre. These were found to be chromite. The existence of crystallised chromite in meteoric irons has hitherto not been completely established. The only instance appears to be recorded by Shepard in the iron of the Seneca River. The above percentage composition is approximately that of the Trenton, Rio Juncal, Seneca River, and Staunton irons.

B. H. B.

So-called Northport Meteorite. By F. C. ROBINSON (*Amer. J. Sci.*, 35, 212—213).—A specimen of a black stone described as a meteorite which fell in Northport, Maine, gave on analysis the following results:—

Fe.	Al.	Cu.	Mg.	Co.	SiO ₂ .	S.	P.	Total.
43·37	4·19	0·88	2·05	0·25	27·68	1·10	0·03	79·55

Traces of manganese were observed. The magnesium, aluminium, and most of the iron were evidently combined as silicates. The rest of the iron was present as sulphide and oxide, and the copper as

sulphide. Sections under the microscope closely resemble those made from furnace slag. It will be noticed, too, that the analysis corresponds very closely with published analyses of slag. In fact the so-called meteorite is identical in composition with copper-slag from the old Revere Copper Works in Massachusetts. Although there can be no doubt that this specimen is an old copper-slag, still the fall of a meteorite at Northport cannot be questioned, and true meteoric fragments may possibly yet be found there.

B. H. B.

Organic Chemistry.

Fire-damp. By C. WINKLER (*J. pr. Chem.* [2], **37**, 254—258).—This is a controversial paper, in which the author states that many of the opinions advanced by Franke (this vol., p. 570) are not in accordance with those held by experts. G. T. M.

Allylene. By A. BÉHAL (*Bull. Soc. Chim.*, **48**, 788—799).—A number of experiments, made with a view to prepare symmetrical allylene, are described. The compounds employed were allyl iodide, trimethylene bromide, allyl alcohol, α - and β -epidichlorhydrin, &c.

The experiments of Aarland (*J. pr. Chem.* [2], **6**, 256) on the electrolysis of itaconic acid were repeated, but only negative results were obtained, from which the author concludes (1) that allylene, $\text{CH}_2\text{:C:CH}_2$, has not yet been isolated; (2) that it is possible that the compound is not capable of existing. Further, it is pointed out that the reactions hitherto employed for preparing allylene—(Hartenstein acted on β -epichlorhydrin with sodium (*J. pr. Chem.* [2], **7**, 310)—ought to yield not this substance, but closed-chain compounds.

N. H. M.

Trichloralcohol: Action of Zinc Ethide on Aldehydes. By M. DELACRE (*Bull. Soc. Chim.*, **48**, 784—788).—40 grams of zinc ethide are dissolved in about 700 c.c. of absolute ether and gradually treated with an ethereal solution of 51 grams of chloral. After 24 hours, crystals of the compound $\text{ZnEtO}\cdot\text{CH}_2\text{CCl}_3$ separate. If 48 grams of chloral is now added to the mixture, a further reaction takes place, and zinc trichlorethoxide, $\text{Zn}(\text{O}\cdot\text{CH}_2\text{CCl}_3)_2$, separates as an abundant, white, pulverulent precipitate.

Phosphorus trichloride acts on trichloralcohol with liberation of hydrogen chloride and formation of *trichlorethyl phosphite*. This is a clear liquid which fumes only slightly when freshly distilled.

Phosphorus pentachloride reacts with trichloralcohol, yielding the compound $\text{CCl}_3\cdot\text{CH}_2\text{Cl}$; to complete the reaction, the mixture is afterwards heated at 140° . The new compound has an aromatic odour, melts at 73 — 74° , and sublimes; it is very soluble in ether, sparingly soluble in light petroleum.

N. H. M.

Constitution of Guthrie's Chlorethyl Bisulphide. By W. SPRING and A. LECRENIER (*Bull. Soc. Chim.*, **48**, 629—630).—By the action of sulphur chloride on ethylene, Guthrie obtained (*Annalen*, **119**, 91, and **121**, 108) the two compounds $S_2(C_2H_4Cl)_2$ and $S_2(C_2H_3Cl_2)_2$. When the former compound is oxidised with nitric acid, β -chloroethylsulphonic acid is formed, the lead salt of which when heated with ammonia yielded taurine. The constitution of Guthrie's compound is therefore $S_2(CH_2\cdot CH_2Cl)_2$. N. H. M.

Cyanogen Compounds of Sulphines. By G. PATEIN (*Compt. rend.*, **106**, 861—863).—The author has prepared the iodides of the sulphines, SMe_3I , SEt_3I , $SMeEt_2I$, and SMe_2EtI , which will be described subsequently. The sulphur seems to play the same part as the nitrogen in ammonia.

If the hydriodide of triethylsulphine iodide is dissolved in alcohol at 90° , and mixed with silver cyanide, some heat is developed, and if the product is filtered and the filtrate evaporated in a vacuum, the compound $SEt_3Cy, AgCy$ is obtained in crystals. These are dissolved in alcohol and mixed with ether, when a syrupy liquid is precipitated which crystallises in a vacuum over sulphuric acid. The corresponding methyl compound is obtained in a similar manner and crystallises in long needles. The compounds $SMeEt_2Cy, AgCy$ and $SMe_2EtCy, AgCy$ were also prepared. They all crystallise well and are soluble in alcohol in almost all proportions, but are insoluble in ether. They melt readily without decomposition, but at 2° or 3° above the melting point the sulphine cyanide volatilises and silver cyanide is left. All except the trimethyl compound are deliquescent, and the attraction for water increases with the number of ethyl groups. They are partially decomposed by water with separation of silver cyanide. When treated with acids, half the cyanogen is evolved as hydrocyanic acid, and a salt of the sulphine is formed, silver cyanide being precipitated. With hydrochloric acid, the silver separates as silver chloride; if the compound is treated with silver nitrate, the whole of the cyanogen is removed in the form of silver cyanide. C. H. B.

Action of Chlorine on the Sulphides of Alcoholic Radicles. Preparation of some new Chlorine-derivatives. By W. SPRING and A. LECRENIER (*Bull. Soc. Chim.*, **48**, 623—628).—When sulphur derivatives (sulphides, hydrosulphides, and bisulphides) of propyl, isobutyl, and amyl are treated with dry chlorine in diffused daylight, in presence of a little iodine, reactions take place with considerable development of heat, causing the liquids to boil. No chlorinated sulphides are formed, the sulphur being eliminated as dichloride; much hydrogen chloride is evolved.

In the case of propyl sulphide, the two chlorides $C_3H_7Cl_2$ and $C_3H_5Cl_2$ are obtained. The former compound, which had not been previously prepared, is a liquid boiling at 145 — 150° ; its constitution was determined by heating it with silver oxide and water, when it yields silver chloride and propionate.

Isobutyl sulphide yielded the dichloride $C_4H_9Cl_2$, boiling at 105° , a

new *trichloride*, CPrCl_3 , and a crystalline tetrachloride, $\text{C}_4\text{H}_6\text{Cl}_4$. Amyl sulphide gave a mixture of six chlorides:— $\text{C}_5\text{H}_{11}\text{Cl}$, $\text{C}_4\text{H}_7\cdot\text{CHCl}_2$, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CCl}_3$, $\text{C}_5\text{H}_9\text{Cl}_4$, a *pentachloride*, $\text{CHMe}_2\cdot\text{CCl}_2\cdot\text{CCl}_3$, and a *hexachloride*, probably $\text{CMe}_2\text{Cl}\cdot\text{CCl}_2\cdot\text{CCl}_3$.
N. H. M.

Trimethylene: Formation of Allyl Alcohol from Symmetrical Dichlorhydrin. By H. TORNÖE (*Ber.*, 21, 1282—1291).—Trimethylene was prepared by the action of zinc-dust on trimethylene bromide in presence of alcohol.

Allyl alcohol was obtained by the method of Hübner and Müller, by the action of sodium on symmetrical dichlorhydrin. The dichlorhydrin must always be in excess, and should be kept cold by means of ice and hydrochloric acid. The yield is about 50 per cent. of the theoretical. To free it from chlorine, it is heated at 70° with potash, when an oil of the formula $(\text{C}_{10}\text{H}_{18}\text{O}_4)_n$ is formed. This boils at 227 — 229° . Allylthiocarbamide melts at 78.4° , and is sparingly soluble in ether.

Allyl carbamate, $\text{C}_4\text{H}_7\text{NO}_2$, is prepared by passing carbonyl chloride through allyl alcohol and treating the fractionated product with ammonia. It is readily soluble, melts at 21.5 — 22° and boils at 203 — 204° . Preparations were made from ordinary allyl alcohol and from allyl alcohol prepared as given above.

When pure dichlorhydrin from epichlorhydrin is reduced with 5 per cent. sodium amalgam, a few drops of allyl alcohol is formed, the chief product being an oil which boils at 114° . When this is treated with dry hydrogen chloride, it is converted into symmetrical dichlorhydrin. The oil was therefore epichlorhydrin. When this is treated with sodium amalgam, the greater part remains unchanged; a few drops of allyl alcohol are formed but no isopropyl alcohol. (Compare Buff, *Annalen*, Suppl. 5, 242).
N. H. M.

Oxidation of Olefines and of Alcohols of the Allyl Series. By G. WAGNER (*Ber.*, 21, 1230—1240).—Olefines yield the corresponding glycols, and alcohols of the allyl alcohol series yield glycerols when oxidised with potassium permanganate in neutral, aqueous solution. The yield of glycol is about 50 per cent., that of the glycerol in some cases about 80 per cent., of the theoretical quantity.

Isobutylene yields the glycol, part of which is further oxidised to hydroxyisobutyric acid; the latter then decomposes into acetone and formic acid, part of the acetone being further oxidised to acetic acid. (Compare O. and F. Leidler, *Abstr.*, 1879, 907.)

Isopropylethylene gives the corresponding glycol, which is partially converted into isobutylformic acid; the latter splits up into formic acid and isobutaldehyde, which is further converted into acetone and acetic acid. (Compare Leidler, this *Jour.*, 1877, ii, 421.)

Ethylene yields the glycol and formic acid.

Trimethylethylene, prepared from the iodide of tertiary amyl alcohol, gives a mixture of trimethylethylene glycol and unsymmetrical methylethylene glycol, which shows that two olefines are produced by acting on the tertiary iodide with alcoholic potash.

Acetone, a few drops of a higher boiling compound, and acetaldehyde were also obtained.

Isodibutylene yields small quantities of oxoctenol, and a glycol which boils at 216—218° and crystallises from light petroleum in shining, well-defined rhombohedrons melting at 59·5°.

Trimethylene is not oxidised by potassium permanganate, but diallyl yields a tetrahydroxy-alcohol, and pinene yields a dihydroxy-alcohol.

Allyl alcohol, ethylvinyl carbinol, allylisobutyl carbinol, methylallyl carbinol, and dimethylallyl carbinol, all give the corresponding glycerol. F. S. K.

Derivatives of Acetylacetone: Synthesis of Polyatomic Alcohols. By A. COMBES (*Bull. Soc. Chem.*, **48**, 474—483).—An aqueous solution of acetylacetone is treated with a little hydrochloric acid, and then with 1 per cent. sodium amalgam in small amounts, the liquid being always kept acid. After some days the whole is treated with a large excess of potassium carbonate, and extracted with chloroform. The extract contains two compounds, amylic glycol and the anhydride of a tetratomic alcohol, which are separated by fractional distillation.

Normal amylic glycol, $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, is a colourless liquid of a rather agreeable odour boiling at 177°. When cooled, it becomes syrupy; it is very soluble in water.

The *anhydride*, $\begin{array}{c} \text{OH}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CMe} \\ | \quad | \\ \text{OH}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CMe} \end{array} \text{O}$, is a yellowish liquid having an odour resembling that of glycol, and boils at about 270°.

When acetylacetone is heated with hydriodic acid (sp. gr. 1·8) at 180—185° for some hours, it is converted into normal pentane. If less concentrated hydriodic acid is used, and a temperature of 100—105°, the two iodides $\text{CHMeI}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Me}$ and $\text{CH}_2\cdot(\text{CHMeI})_2$ are obtained.

Acetylacetone hexachloride, $\text{CH}_2(\text{CO}\cdot\text{CCl}_3)_2$, is prepared by saturating the cold ketone with chlorine; the product is heated in a retort exposed to sunlight, dry chlorine is passed through it for several days, and the dense liquid is washed with water. It is colourless, has a pungent odour, and is very irritating to the eyes; it boils at 190—200° under 20 mm. pressure. When treated with dilute aqueous soda, trichloroacetone is formed. Ammonia acts on it with formation of much chloroform, together with some acetamide.

Acetylacetone hexabromide, $\text{CH}_2(\text{CO}\cdot\text{CBr}_3)_2$, obtained by treating acetylacetone with 13 times its weight of bromine, crystallises in colourless needles melting at 107—108°. It resembles the hexachloride in its behaviour towards alkalis.

When dry ammonia is passed through acetylacetone dissolved in ether, the compound $\text{NH}_4\cdot\text{CH}(\text{COMe})_2$ separates in colourless spangles; it is very unstable, and decomposes into acetylacetone and ammonia when exposed to air; if heated in a closed tube at 25—30°, it yields a mixture of acetone and acetamide.

Amines react with acetylacetone with formation of nitrogenous compounds. N. H. M.

Levulose. By A. HERZFELD (*Annalen*, **244**, 274—295).—Most of the contents of this paper have already appeared (Abstr., 1886, 438, 862). The author confirms Scheibler's statement (Abstr., 1884, 574) that the reduction of levulose to mannitol by sodium amalgam is, in the first instance, due to the action of the sodium hydroxide on the levulose, and, secondly, to the action of the nascent hydrogen on the decomposition products. Levulose is not reduced by nascent hydrogen in acid solutions. W. C. W.

Isodulcitol. By B. RAYMAN and J. KRUIS (*Chem. Centr.*, 1888, 6, from *Listy. Chem.*, **12**, 7—11).—The striking similarity of quercite to glucose led the authors to determine whether the sugar obtained from the bark of the yellow oak did not actually contain glucose. The phenylhydrazine hydrochloride reaction showed the presence of a glucose in all portions of the sugar. Its reactions with hydrochloric acid very much resemble those of arabinose, the methyl ether of which it might be. When heated with hydriodic acid at 120°, however, no methyl iodide is formed. As it is shown that the reactions described by Raymann (Abstr., 1887, 906) are themselves applicable to isodulcitol, and as the analogy of the sugar $C_6H_{12}O_5$ to the dextrose series is brought into prominence, the authors propose to call it *rhamnose*, because it also appears to be identical with the sugar obtained by Liebermann from *Rhamnus*, the term isodulcitol being retained exclusively for the hexatomic alcohols. With solutions containing 15 to 30 grams, the rotatory power of rhamnose remains unchanged, $[\alpha]_D = +9.3$; fresh solutions are more active, $[\alpha]_D = +12.3$ to $+13$. In alcoholic solution, the specific rotatory power decreases as the relation of alcohol to sugar increases, until a point is reached at which the rotatory power is *nil*; from this point it becomes *lævorotatory*. The authors explain this phenomenon by assuming that rhamnose contains a carbonyl-group which is combined with water, so that the sugar $C_6H_{12}O_5 \cdot H_2O$ contains the group $:C(OH)_2$, which in watery solution remains unchanged, and is symmetrical. In alcoholic solution, however, the attraction of the carbonyl for water is destroyed, and the alcohol reacts with the carbonyl forming the group $:C(OH) \cdot OEt$, which is asymmetric. This group they consider causes the *lævorotatory* action. This supposition has some support, the authors consider, from the fact that rhamnose when dehydrated by boiling with absolute alcohol increases in weight to the extent of $\frac{1}{8}$.

J. P. L.

Molecular Weight of Raffinose. By H. DE VRIES (*Compt. rend.*, **106**, 751—754).—The author has determined the isotonic coefficient of raffinose by the method previously described (Abstr., 1884, 1065), using the middle ribs of the leaves of *Tradescantia discolor*. A solution containing 5.957 per cent. of raffinose is isotonic with a solution of saccharose containing 0.1 gram-molecule per litre. It follows that the molecular weight of raffinose is about 595.7, and this result agrees with the molecular weight of 594, corresponding with the formula $C_{18}H_{32}O_{16} + 5H_2O$ adopted by Loiseau and by Scheibler.

C. H. B.

Inactose of Neutral Sugar. By E. J. MAUMENÉ (*Bull. Soc. Chim.*, **48**, 773—777).—40 grams of a mixture of equal parts of sugar and of freshly-fused silver nitrate (free from acid) is dissolved in 100 c.c. of water; after 24 hours, the solution acquires a dark brown colour, which increases a little when the solution is heated on a water-bath. The product is filtered, and evaporated on a water-bath, when a colourless substance is obtained resembling the hydrate of phosphoric acid. When heated above 140° , it becomes gradually turbid, and water is given off. The filtered liquid has no rotatory power. The name *inactose* is ascribed to the new sugar. To obtain it free from silver, it is treated with a little calcium chloride, and filtered; alcohol is then added to the solution, which on evaporation under a glass cover deposits the sugar; this is washed with a little alcohol, redissolved, and the solution again evaporated as before. It forms a syrup, and could not be obtained in crystals. It unites with lime, but the compound produced is decomposed by carbonic anhydride, and the sugar so recovered is inactive as before. When a mixture of equal weights of sugar and silver nitrate is heated at 150 — 155° from two to three hours, a rather large amount of hexenenic acid is formed. N. H. M.

Iodide of Starch. By H. B. STOCKS (*Chem. News*, **57**, 183).—Moist iodide of starch was employed in the previous experiments (this vol., p. 126). Dry iodide of starch, prepared by adding iodine solution to starch-paste in water, precipitating with alcohol, filtering, and drying, is a black, lustrous substance, which is not decomposed by sunlight nor by heating at 100° , but at somewhat higher temperatures gives off tarry matter and iodine. It does not dissolve in water, and is decomposed by it only after prolonged boiling. Further experiments show that when free iodine acts on silver salts, some silver iodate is formed, and, moreover, tend to confirm the statement that the formation of iodide of starch is due to free iodine (*loc. cit.*). The author finds that the colour of iodide of starch varies with the proportion of iodine employed, but does not vary with different starches. Small quantities of iodine give an indigo-blue colour, larger quantities violet, whilst with an excess of iodine, the colour appears green, although the precipitated iodide is blue.

The colour is destroyed by permanganate, which attacks the starch; by iron filings, and by heating with alcohol, ethyl iodide being formed. Bromine destroys it by the formation of iodine bromide, the latter can be decomposed by carefully neutralising with sodium carbonate, and then the liberated iodine regenerates the blue colour. The iodide is precipitated, but not destroyed, by potassium dichromate. Zinc and sulphuric acid do not act on the colour. D. A. L.

Vinylamine. By S. GABRIEL (*Ber.*, **21**, 1049—1057).—*Vinylamine picrate*, $\text{CH}_2\text{:CH}\cdot\text{NH}_2\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, is formed when the reaction product of moist silver oxide and an aqueous solution of bromethylamine hydrobromide is distilled with steam, the distillate saturated with hydrochloric acid, and a solution of picric acid added. On standing, yellow needles, or short, compact forms separate. It crystallises from

water in fine needles, which, after previously softening, melt at 142° to a reddish-yellow, blistered, glassy mass. When distilled with water, it yields an aqueous solution of vinylamine. *Vinylamine platino-chloride*, $(C_2H_5N)_2H_2PtCl_6$, crystallises in small, well-defined forms, which are readily soluble in water, but only very sparingly or not at all in alcohol. In an aqueous solution of this salt, Nessler's solution gives a yellowish-white precipitate. *Vinylamine bismutho-iodide*, $(C_2H_5NH\dot{I})_3 \cdot 2BiI_3$, crystallises in shining, fiery-red, microscopic, regular, hexagonal leaves, which are almost insoluble in water and dilute acids. *Vinylamine aurochloride* forms flat, golden-yellow needles or plates. The readiness with which solutions of vinylamine platino-chloride and aurochloride decompose is not due to the presence of the metallic chloride. An aqueous solution of the hydrochloride is completely decomposed on heating; an aqueous solution of the free base decomposes in the cold.

When an aqueous solution of vinylamine is neutralised with hydrochloric acid and evaporated at 50° or in a vacuum, a colourless syrup is obtained which contains the hydrochloride of a new base. This base yields a picrate which appears to be identical with β -hydroxyethylamine picrate (this vol., p. 440) and also with the picrates of the bases obtained by the action of potash on chlorethylamine and bromethylamine hydrochloride.

β -Chlorethylamine hydrochloride is obtained by evaporating a solution of vinylamine with a large excess of hydrochloric acid; β -bromethylamine hydrobromide is produced in a similar manner.

β -Iodethylamine hydriodide, $CH_2I \cdot CH_2 \cdot NH_2 \cdot HI$, crystallises from hot, absolute alcohol in colourless, rhombic forms, which, after previously softening, melt and turn brown at 192 – 194° . It is readily soluble in water, and when treated with potash yields a disagreeably smelling oil which is soluble in water.

The *picrate*, $C_2H_5IN, C_6H_3N_3O_7, \frac{1}{2}H_2O$, crystallises in short, compact, yellow prisms, which, after previously softening, melt at about 105° . On heating slowly, they lose water of crystallisation, and then melt at 129 – 131° .

By evaporating a solution of vinylamine with excess of sulphuric acid, a syrup is obtained which crystallises from water in transparent rhombohedra having the composition $C_2H_7NSO_4$. This compound is readily soluble in warm water, softens above 230° , turns brown, and melts when heated on platinum foil, giving out an empyreumatic odour; on igniting, a carbonaceous residue is obtained.

F. S. K.

Action of Zinc-dust on Chloral. By K. CHODOUNSKY (*Chem. Centr.*, 1888, 74, from *Listy. Chem.*, 12, 57–59).—Chloral was allowed to fall drop by drop on to zinc-dust in a retort heated on an oil-bath and attached to a cooled receiver. At 100° the reaction is feeble, but above 120° it becomes very violent, so violent that part of the carbon separated in the reaction is carried over into the receiver. Carbonic oxide was formed, but no chloroform. Chloral was also heated with zinc-dust and zinc oxide in sealed tubes previously filled with carbonic anhydride. In the tubes containing zinc-dust heated at 120° , carbonic

oxide, hydrogen, chloroform, and a product of lower boiling point (probably a lower chlorinated methane), besides carbon and zinc chloride, were found. In the zinc oxide tube, under the same conditions, much gas, zinc chloride, and the zinc salt of an organic acid were found, but no chloroform. In tubes containing zinc-dust and chloral heated at 160°, carbonic oxide, hydrogen, and acetylene were formed, and the liquid consisted of unchanged chloral and traces of chloroform.

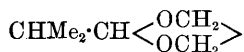
Zinc formate when heated in a retort gave carbonic oxide, hydrogen, carbonic anhydride, zinc oxide, and a little zinc. It appears that chloral is converted by zinc-dust partly into chloroform and zinc formate, and the latter into carbonic anhydride, carbonic oxide, and hydrogen. Chloroform also suffers partial decomposition, which increases with the temperature. J. P. L.

Action of Chloral Hydrate and Iodoform on Mercuric Salts. By S. COTTON (*J. Pharm.* [5], 16, 481—483).—Chloral hydrate reduces mercuric acetate with evolution of carbonic anhydride and formation of mercurous acetate, whilst the same reagent with mercuric nitrate forms carbonic anhydride and mercurous chloride. Iodoform reduces mercuric acetate with evolution of carbonic anhydride and formation of mercurous acetate precisely in the same manner as chloral hydrate does, but iodoform does not reduce mercuric nitrate, its action being limited to the formation of the corresponding iodide. Chloroform and bromoform act on neither of these two salts. J. T.

Compounds of Glycol with some Aldehydes. By H. LOCHERT (*Bull. Soc. Chim.*, 48, 337—338, and 716—718).—*Ethylene ænanthylidene oxide*, $C_6H_{13} \cdot CH \begin{smallmatrix} OCH_2 \\ OCH_2 \end{smallmatrix}$, is prepared (1) by heating ænanthaldehyde (1 vol.) and glycol (3 vols.) for eight days at 125—130°, the upper layer of the product being then fractionally distilled; (2) by heating as in (1) a mixture of ænanthaldehyde (1 vol.), glycol (2 vols.), and glacial acetic acid (1 vol.). The mixing of the glycol and α -aldehyde gives rise to considerable development of heat. It is a mobile liquid, boiling at about 180°, and having an odour resembling that of ænanthaldehyde but less pronounced.

From glycol and valeraldehyde the compound $C_4H_9 \cdot CH \begin{smallmatrix} OCH_2 \\ OCH_2 \end{smallmatrix}$ was obtained. This boils at about 142°, and has an agreeable ethereal odour.

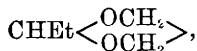
When a mixture of glycol (2 mols.) and isobutaldehyde (1 mol.) is heated in a water-bath for seven days, the compound



is obtained. It is a colourless, refractive liquid, boiling at 124—126°, soluble in 10 parts of water, very soluble in alcohol and ether. When heated in a closed tube at 140° for two days, it is decomposed into its

original constituents. Caustic potash and dry alkalis have no action on it.

Propaldehyde and glycol yield the condensation product



a colourless liquid having an odour resembling that of propaldehyde and boiling at 105—107°. N. H. M.

Action of Bromine on the Compounds of Glycol with Aldehyde. By H. LOCHERT (*Bull. Soc. Chim.*, **48**, 718—719).—Bromine reacts with the compounds of aldehydes with glycol (preceding Abstract), yielding monobromo-derivatives.

Acetoacetaldehyde. By L. CLAISEN and N. STYLOS (*Ber.*, **21**, 1144—1149).—The sodium compound of acetoacetaldehyde,



is obtained by adding a mixture of acetone (1 mol.) and ethyl formate (1 mol.) to sodium ethoxide (1 mol.) free from alcohol and suspended in anhydrous ether cooled in ice. It is very soluble in water, gives a dark yellowish-red coloration with ferric chloride, and on treatment with copper acetate yields the copper salt $(\text{C}_4\text{H}_5\text{O}_2)_2\text{Cu}$, which crystallises in bright blue needles, and is soluble in hot benzene and ether. The *anilide*, *toluidide*, and *naphthalide* were also prepared. The *benzene-azo-derivative*, $\text{COH} \cdot \text{CHAc} \cdot \text{N}_2\text{Ph}$, is crystalline, and melts at 117—118°. Addition of phenylhydrazine to the concentrated aqueous solution of the sodium salt free from acetone converts it into a *methylphenylpyrazole* (? Ph : Me = 1 : 5), which has a sp. gr. = 1.081 at 15°, boils at 254—257°, and is probably identical with that obtained from ethyl acetopyruvate (this vol., p. 676). It is, however, solid at the ordinary temperature, and melts at 36—37°. Acetoacetaldehyde could not be isolated owing to its tendency to undergo condensation with the formation of symmetrical triacetylbenzene.

1 : 3 : 5 *Triacetylbenzene*, $\text{C}_6\text{H}_3\text{Ac}_3$, is obtained by treating the above product with a small quantity of ice-cold water, separating the upper ethereal layer, and treating the lower aqueous layer with an equivalent quantity of acetic acid. It crystallises in small, white needles, melts at 162—163°, is readily soluble in acetic acid, sparingly soluble in alcohol, ether, and water, and on oxidation with concentrated nitric acid is converted into trimesic acid.

The following compounds were prepared by Meyerwitz:—*Sodium propionylacetaldehyde*, $\text{COEt} \cdot \text{CHNa} \cdot \text{COH}$, and the corresponding *ethyl phenylpyrazole*, $\text{C}_{11}\text{H}_{12}\text{N}_2$, a colourless liquid boiling at 273—275°, and having a sp. gr. = 1.064 at 15°; *sodium butyrylacetaldehyde*,



its copper salt crystallising in flat, greenish prisms, and the corresponding *pyrazole*, $\text{C}_{12}\text{H}_{14}\text{N}_2$, a colourless oil boiling at 279—281° and having a sp. gr. = 1.0435 at 15°; *sodium heptylacetaldehyde*,



and the corresponding *pyrazole*, $C_{16}H_{20}N_2$, a thick oil boiling at 318—320°.

W. P. W.

Action of Carbonyl Chloride on Sodium Formate. By R. OTTO (*Ber.*, 21, 1267—1268).—Hentschel (Abstr., 1884, 991) prepared acid anhydrides by the action of carbonyl chloride on the sodium salts of acetic and other acids. The author attempted to prepare formic anhydride by this method, but obtained only sodium chloride, carbonic anhydride, carbon monoxide, and formic acid. It is probable that formic anhydride is not capable of existing.

N. H. M.

Chloro-derivatives of Ethyl Acetate. By M. DELACRE (*Bull. Soc. Chim.*, 48, 706—716; compare Abstr., 1887, 713).—*Chlorethyl dichloracetate*, $CHCl_2 \cdot COO \cdot C_2H_4Cl$, is prepared by mixing chloroacetic chloride with glycol chlorhydrin in molecular proportion, keeping the whole cool; the mixture is afterwards heated on a water-bath until no more hydrogen chloride is evolved, and precipitated with water; it is then made alkaline, separated, and dried with calcium chloride. It boils at 209—212° under 767 mm. pressure, and has an agreeable, aromatic odour; sp. gr. = 1.200 at 15°.

Chlorethyl trichloracetate, $CCl_3 \cdot COO \cdot C_2H_4Cl$, is obtained from trichloroacetic chloride in a manner similar to the dichloracetate. It has an agreeable, aromatic odour, and boils at 217° under 766 mm. pressure; sp. gr. = 1.251 at 15°.

Dichlorethyl monochloracetate, $CH_2Cl \cdot COO \cdot C_2H_3Cl$, prepared by distilling a mixture of dichlorethyl alcohol and chloroacetic chloride, boils at 215° (corr.) under 760 mm. pressure; sp. gr. = 1.216 at 15°.

Dichlorethyl dichloracetate, $CHCl_2 \cdot COO \cdot C_2H_3Cl$, boils at 223° under 756 mm. pressure; sp. gr. = 1.25 at 15°.

Dichlorethyl trichloracetate, $CCl_3 \cdot COO \cdot C_2H_3Cl$, boils at 230° under 760 mm. pressure; it could not be solidified.

Trichlorethyl acetate (Thurnlackh, Abstr., 1882, 295) boils at 170° (corr.) under 747 mm. pressure; sp. gr. = 1.189 at 15°.

Trichlorethyl chloracetate, $CH_2Cl \cdot COO \cdot C_2H_2Cl_3$, is obtained by heating for some time and then distilling a mixture of acetic chloride and trichlorethyl alcohol. It boils at 220° (corr.) under 767 mm. pressure. When freshly distilled, it has a slightly acid odour, which changes to a feebly aromatic odour; sp. gr. = 1.25 at 15°.

Trichlorethyl dichloracetate, $CHCl_2 \cdot COO \cdot C_2H_2Cl_3$, boils with slight decomposition at 230—231° under 767 mm. pressure; sp. gr. 1.267 at 15°. When kept, it decomposes with evolution of hydrogen chloride.

Trichlorethyl trichloracetate, $CCl_3 \cdot COO \cdot C_2H_2Cl_3$, boils at 236° under 767 mm. pressure with slight liberation of hydrogen chloride. It is crystalline, and melts at 24—26°; when kept, it melts at the ordinary temperature, a little hydrogen chloride being given off.

When acetic chloride and acetaldehyde are mixed, the temperature of the mixture rises to 60° or 80°; with paraldehyde, cold is first produced, and then a development of heat takes place in consequence of the reaction between the acetic chloride and depolymerised aldehyde.

Acetic chloride reacts with anhydrous dichloraldehyde with formation of the compound $CH_3 \cdot COO \cdot CHCl \cdot CHCl_2$. This boils at 185°, has a

fruity odour, and gives off hydrogen chloride when kept. With acetic chloride (2 mols.) and the hydrate of dichloraldehyde the compound $\text{CHCl}_2\cdot\text{CH}(\text{OAc})_2$ is obtained; this melts at 52° and boils at $220\text{--}222^\circ$.

When chloracetic chloride and dichloraldehyde (22 grams of each) are heated at 150° for 18 hours, the compound $\text{CCl}_3\cdot\text{COO}\cdot\text{CHCl}\cdot\text{CHCl}_2$ is formed. It is a colourless liquid of aromatic odour, boiling at $226\text{--}228^\circ$ under 756 mm. pressure. N. H. M.

Volatile Acids of Suint. By A. BUISINE (*Bull. Soc. Chim.*, **48**, 639—642).—The acids present in suint do not pre-exist in the perspiration, but are formed under the influence of microbes; the maximum amount of acids is found after 8 to 10 days' fermentation. In order to obtain the acids, the liquid is evaporated to dryness, the residue extracted with alcohol, and the alcoholic solution evaporated; the residue is dissolved in water, acidified with phosphoric acid, steam distilled, and the amount of acid determined by titration. The separation and determination of the amounts of the various acids are effected by converting the mixed acids into ethyl salts and fractionally distilling. The following numbers show the relative amounts:—Acetic acid (60); propionic acid (25); butyric acid (5); valeric acid (4); caproic acid (3); and benzoic acid (3). Formic and caprylic acids and phenol are present only in traces.

The amount of propionic acid in 1 cub. metre of suint water is about 5 or 6 kilos. (compare *Bull. Soc. Chim.*, **46**, 479).

N. H. M.

Millet Oil and some of its Products of Decomposition. By G. KASSNER (*Arch. Pharm.* [3], **25**, 1081—1101).—The oil of millet was treated with lead oxide, the product freed from water, and treated with ether. The solution after being filtered was shaken with sulphuric acid, separated, and evaporated. The oil is then kept in a closed vessel over pyrogallol and potash as it absorbs oxygen. Analyses of the acid and salts pointed to the formula $\text{C}_{18}\text{H}_{32}\text{O}_3$. It is probable that this hydroxy-acid is a product of oxidation of an acid, $\text{C}_{18}\text{H}_{32}\text{O}_2$, existing in millet.

When the oil of millet is oxidised with potassium permanganate, the acid $\text{C}_6\text{H}_{12}\text{O}_2$, probably *isobutylacetic acid*, and two acids, $\text{C}_6\text{H}_{11}\text{O}_2\cdot\text{OH}$ and $\text{C}_{14}\text{H}_{26}\text{O}_2(\text{OH})_2$, are formed. The former hydroxy-acid crystallises in plates melting at $107\text{--}108^\circ$, readily soluble in water, and yields an *acetyl-derivative*, which melts at $70\text{--}71^\circ$. The acid, $\text{C}_{14}\text{H}_{26}\text{O}_2(\text{OH})_2$, melts at 60° , is insoluble in water, readily soluble in alcohol and ether. The *alkali salts* are readily soluble, and could not be obtained in crystals.

When millet oil is fused with potash, acetic, lauric, and in small quantity butyric and oxalic acids are formed. When distilled, it yields an *acid*, $\text{C}_9\text{H}_{16}\text{O}_2$ or $\text{C}_{10}\text{H}_{18}\text{O}_2$, which boils at $216\text{--}220^\circ$.

The following partially-developed constitutional formulæ are suggested for the hydroxy-acid and the millet-oleic acid, from which it is supposed to be derived:—



N. H. M.

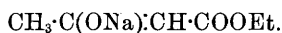
Oil from the Seeds of *Curcas Purganus* (formerly *Jatropha Curcas*). By F. M. HORN (*Zeit. anal. Chem.*, **27**, 163—165).—This oil, formerly employed as a purgative under the names *Oleum ricini majoris*, *Oleum infernale*, is at the present time much used for burning and for soap making, also for adulterating olive oil, and seemingly for making Turkey-red oil. It begins to crystallise at 9°, and is completely solid at 0°. At 15° its sp. gr. is 0.9192. It differs from castor oil in its very sparing solubility in alcohol. It appears to saponify readily in the cold, but in reality forms only acid soaps; for complete saponification heat is required, and solid potash acts better than solution.

It gives for Hehner's number, 87.9; for Reichert's, 0.65; for Köttstorfer's, 230.5; and for Hübl's, 127. M. J. S.

Constitution of Ethyl Sodacetoacetate and Ethyl Sodaceto-malonate. By A. MICHAEL (*Amer. Chem. J.*, **10**, 158—160).—Ethyl acetylmalonate has been prepared by Ehrlich, Conrad, and Guthzeit, from ethyl sodacetoacetate and ethyl chlorocarbonate, and lately by Lange from acetic chloride and ethyl sodiomalonate. But the acetates prepared by these two methods are not identical; the one being insoluble in strong cold alkaline solutions, the other being very readily soluble in any alkali, and boiling also 5° lower; moreover, in the latter process, ethyl diacetylmalonate is formed at the same time.

From these data it is concluded that whilst ethyl acetoacetate is correctly represented by the formula $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COOEt}$, the corresponding sodium compound is $\text{CH}_3\cdot\text{C}(\text{ONa})\cdot\text{CH}\cdot\text{COOEt}$, and the substance obtained from it by the action of ethyl chlorocarbonate is $\text{CH}_3\cdot\text{C}(\text{O}\cdot\text{COOEt})\cdot\text{CH}\cdot\text{COOEt}$. This certainly explains why the substance has no distinct acid properties like the real ethyl acetylmalonate, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{COOEt})_2$.

Further, Conrad and Guthzeit have prepared ethyl methenyltricarboxylate by the action of ethyl chlorocarbonate on ethyl sodiomalonate, and ascribe to it the constitution $\text{CH}(\text{COOEt})_3$, and yet it is at once decomposed by alkalis and has no acid properties. The ethyl sodiomalonate used by these authors was first prepared in the solid state; but if ethyl chlorocarbonate is at once added to the product of the action of sodium on ethyl malonate, then a substance is obtained which has acid properties, forms a very stable sodium salt, and is doubtless expressed by the above formula, whilst the compound of Conrad and Guthzeit is $\text{OEt}\cdot\text{C}(\text{O}\cdot\text{COOEt})\cdot\text{CH}\cdot\text{COOEt}$. This and the above constitutional formula for ethyl sodacetoacetate is explained on the assumption that sodium acting on ethyl malonate or ethyl acetoacetate forms at first sodium salts expressed by the usual formulæ, $\text{COOEt}\cdot\text{CHNa}\cdot\text{CO}\cdot\text{OEt}$ and $\text{CH}_3\cdot\text{CO}\cdot\text{CHNa}\cdot\text{COOEt}$, but that owing to the affinity of sodium for oxygen, these are converted by heat, &c., into $\text{OEt}\cdot\text{C}(\text{ONa})\cdot\text{CH}\cdot\text{COOEt}$ and



The action of sodium on isatin is probably similar.

H. B.

Acetoacetic Acid and Ethyl Succinosuccinate. By A. HANTZSCH and F. HERRMANN (*Ber.*, **21**, 1084—1085).—A reply to the article by Geuther (this vol., p. 579).

Condensation Products of Urethane and Ethyl Acetoacetate. By J. MEISTER (*Annalen*, **244**, 233—253).—A condensation product of the composition $C_9H_{15}NO_4$ is prepared by heating at 140° in sealed tubes a mixture of urethane (10 grams), ethyl acetoacetate (20 grams), ether (10 grams), and a small quantity of ammonium chloride. It is easily decomposed by acids: thus with strong hydrochloric acid it yields ammonia, acetone, ethyl chloride, and carbonic anhydride.

As this substance is also formed by the action of ethyl chlorocarbonate on ethyl paramidoacetoacetate, it may be regarded as ethyl β -amidocrotonate, in which an atom of hydrogen is displaced by the group $COOEt$. Its constitution is represented by the formula $COOEt \cdot NH \cdot CMe \cdot CH \cdot COOEt$. It is not attacked by aqueous solutions of the alkalis, but is saponified by alcoholic potash, yielding an oily liquid of the composition $C_{12}H_{23}NO_6$.

A tribromo-derivative, soluble in alcohol and in ether, is obtained by the action of bromine on the condensation product suspended in water, but a corresponding trichloro-derivative could not be obtained.

At 160° , alcoholic ammonia acts on the condensation product, and crystals of the composition of β -uramidocrotonamide, containing 1 mol. of alcohol, are deposited. The crystals melt at 131° , and are soluble in hot alcohol. The same compound is formed by the action of alcoholic ammonia on ethyl β -uramidocrotonate. A corresponding anilide could not be prepared. The amide is decomposed by water, yielding urea, ammonia, acetone, alcohol, and carbonic anhydride. A strong boiling aqueous solution of potassium hydroxide decomposes the amide, yielding an oily liquid of the composition $C_{11}H_{20}N_2O_4$.

W. C. W.

Antimony Potassium Oxalate. By P. KAY (*Chem. News*, **57**, 193—194).—Two samples of this substance were found to correspond respectively with the formulæ $K_4Sb_2(C_2O_4)_3 + 3H_2O$ and $K_3Sb(C_2O_4)_3 + 2H_2O$. The antimony was estimated either by mixing the solution with tartaric acid, neutralising with sodium carbonate, adding potassium carbonate, then bleaching powder, and titrating the excess of the latter with sodium arsenite; or by direct titration with potassium hydroxide, using phenolphthaleïn as indicator. The potassium was estimated by converting into carbonate and titrating. The oxalic acid was determined in the usual way.

D. A. L.

Derivatives of Ethylmalonic Acid. By M. FREUND and B. B. GOLDSMITH (*Ber.*, **21**, 1245—1247).—*Ethylmalonamide*,



is obtained by acting on diethyl ethylmalonate with concentrated ammonia. It crystallises from alcohol, and melts at 207 — 208° .

Ethylmalonanilide, $CH_2Et(CONHPh)_2$, produced by heating diethyl ethylmalonate or ethylmalonamide with aniline, crystallises from

alcohol in needles melting at 213—215°. It is insoluble in water, but dissolves readily in alcohol and glacial acetic acid.

Phenylethylmalonamide, $\text{NH}_2\text{CO}\cdot\text{CHEt}\cdot\text{CO}\cdot\text{NHPH}$, obtained by heating 1 mol. of the amide with 1 mol. of aniline, crystallises from water or alcohol, and melts at 182°.

Ethylmalonanilic acid, $\text{COOH}\cdot\text{CHEt}\cdot\text{CO}\cdot\text{NHPH}$, is obtained by boiling the preceding compound with an excess of lime. It is soluble in alcohol, crystallises from water, and melts at 150° with evolution of carbonic anhydride. F. S. K.

Action of Ethyl Oxalate on Acetone. By L. CLAISEN and N. STYLOS (*Ber.*, 21, 1141—1143; compare *Abstr.*, 1887, 917).—A very characteristic bluish-violet colour is formed when ethyl acetoxyruvate is boiled with acetic acid and some sodium acetate. *Copper acetoxyruvate*, $(\text{C}_{17}\text{H}_{25}\text{O}_4)_2\text{Cu}$, crystallises in small, bright-green needles. When the ethyl salt is boiled with phenylhydrazine in acetic acid solution, and the product treated with water, a thick oil is obtained which, after saponification with alcoholic soda, yields a white crystalline precipitate of a *methylphenylpyrazolecarboxylic acid*, $\text{C}_{10}\text{H}_9\text{N}_2\text{COOH}$, on treatment with hydrochloric acid. The acid melts at 96°, but seems to contain either water or alcohol of crystallisation, since the melting point gradually rises to 134—136° by prolonged drying at 80—90°. At 200—210°, the acid loses carbonic anhydride, and is converted into a methylphenylpyrazole probably identical with that prepared from acetoacetaldehyde (this vol., p. 671), and isomeric with that obtained by Knorr (*Annalen*, 238, 202); it has a sp. gr. = 1.085 at 15°, solidifies in a freezing mixture, and boils at 256—257° without decomposition.

Oxalyldiacetone, $\text{CH}_2\text{Ac}\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_2\text{Ac}$, is obtained by adding to a well-cooled mixture of anhydrous ether and sodium ethoxide (2 mols.) free from alcohol, first acetone (2 mols.), and then ethyl oxalate (1 mol.), and allowing the product to remain for two days; the resulting yellow salt is then dissolved in water, and decomposed by the addition of acetic acid. It crystallises in white prisms, melts at 120—121°, is soluble in alcohol, ether, and chloroform, sparingly soluble in light petroleum and cold water, and gives a dark brownish-red coloration with alcoholic ferric chloride. W. P. W.

Derivatives of Saccharic and Mucic Acids. By MAQUENNE (*Bull. Soc. Chim.*, 48, 719—723).—*Tetracetylmucic acid*,



is obtained by boiling mucic acid with acetic anhydride (2 parts) in presence of zinc chloride, until it is dissolved. The product is precipitated with water, washed, and crystallised from alcohol. It forms colourless, efflorescent needles, melting at 266° (corr.), sparingly soluble in water, readily soluble in hot alcohol; its reaction is strongly acid, but it does not form salts.

The lactone of diacetylsaccharic acid, $\text{C}_{10}\text{H}_{10}\text{O}_8$, is prepared by adding strong sulphuric acid, drop by drop, to a mixture of hydrogen potassium saccharate and acetic anhydride (2 parts). The product is

precipitated by water and washed until no longer acid. It melts at 188° (corr.) without decomposition, and is sparingly soluble. It seems to be identical with the compound prepared by Baltzer by the action of acetic chloride on saccharic acid (*Annalen*, **149**, 241).

Saccharic acid diphenylhydrazide, $C_{18}H_{22}N_4O_6$ (Kiliani, this vol., p. 46) is obtained by heating an aqueous solution of saccharic acid, phenylhydrazine hydrochloride (each 8 grams), and sodium acetate (12 grams), on a water-bath for two hours. It is slightly yellow, melts at 210° with evolution of gas, is insoluble in water, alcohol, and ether, soluble in hot alcoholic potash. The diphenylhydrazide of mucic acid (Bülow, Abstr., 1887, 138) was prepared in a similar manner.

N. H. M.

Synthesis of Aspartic Acid. By A. PIUTTI (*Chem. Centr.*, 1888, 68—69, from *Rendi. Acc. Linc.* [4], **3**, 300—303).—Ethyl sodoxalacetate was prepared by treating 25 grams of ethyl oxalate and 15 grams of ethyl acetate dissolved in four times their weight of absolute ether, with 4 grams of sodium in small pieces. From this compound, the oxime was prepared by dissolving molecular proportions of the above compound and hydroxylamine hydrochloride in water, and gently warming. If the oily oxime which separates after a time is dissolved in ether, and the ether evaporated, a colourless oil is left, which soon appears blue or green by reflected, and violet by transmitted light. If a watery solution of this oxime is reduced with sodium amalgam, aspartic acid is formed.

The aspartic acid agrees in its properties with Dessaigne's acid and Piutti's inactive acid. The reduction of the oxime in watery, alcoholic and acetic acid solutions gives rise to highly coloured products, and small quantities of mono- and di-ethyl aspartates. Reduction of a watery solution of the oxime with ammonia also gives a good yield of acid.

J. P. L.

Furfuran-derivatives. By W. MARCKWALD (*Ber.*, **21**, 1398—1404).—The ethyl salt of the bibasic acid, $C_5H_5O(COOEt)_2$, obtained by treating furfuracrylic acid in alcoholic solution with hydrogen chloride (this vol., p. 135), and now termed *ethyl propiononedicarboxylate*, forms an *oxime*, $OH \cdot N : C_5H_5(COOEt)_2$, which crystallises in long, slender, white needles, melting at 38° . It is sparingly soluble in water and light petroleum; readily soluble in most other solvents, and in cold hydrochloric acid and alkalis. The *phenylhydrazone* of propiononedicarboxylic acid, $N_2HPh \cdot C_5H_5(COOH)_2$, crystallises from alcohol in pale-yellow, microscopic crystals, melts at 114.5° , and is insoluble in water, benzene, light petroleum, and chloroform, soluble in ether, and readily soluble in alcohol, acetone, and acetic acid. On heating with excess of hydriodic acid (sp. gr. = 1.7) and the theoretical quantity of amorphous phosphorus at 200 — 220° for many hours, the acid is converted into normal pimelic acid, hence it has the formula $CO(CH_2 \cdot CH_2 \cdot COOH)_2$. The author regards its formation from furfuracrylic acid by the splitting of the furfuran "ring" as an additional argument in favour of the view that furfuraldehyde has the formula $\begin{matrix} <CH:C(COH) \\ <CH:CH->O \end{matrix}$, and not that ascribed to it by Baeyer.

Ethyl hydrogen propiononedicarboxylate, $\text{COOH}\cdot\text{C}_2\text{H}_5\text{O}\cdot\text{COOEt}$, is formed by boiling the ethyl salt with the calculated quantity of alcoholic potash. It crystallises in white needles, melts at $67\text{--}68^\circ$, and is insoluble in light petroleum, soluble in water, readily soluble in alcohol, ether, benzene, chloroform, and carbon bisulphide. The silver salt, $\text{C}_9\text{H}_{13}\text{O}_5\text{Ag}$, decomposes very readily. The *phenylhydrazone*, $\text{C}_9\text{H}_{14}\text{O}_4\cdot\text{N}_2\text{HPh}$, forms pale-yellow, microscopic crystals, melts at 112° , and is insoluble in water and light petroleum, readily soluble in ether, hot alcohol, benzene, and acetic acid.

On digestion with alcoholic ammonia, either for some hours at 100° or for a short time at 150° , ethyl propiononedicarboxylate is converted into a compound, $\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2$, which is probably symmetrical *imido-pimelimide*. It crystallises from hot water in long, thick prisms, from alcohol in long, compact, white needles, begins to sublime rapidly at $250\text{--}260^\circ$ without decomposition, melts at 292° , is sparingly soluble in the ordinary solvents, and decomposes when boiled with hydrochloric acid or alkalis into ammonia and propiononedicarboxylic acid.

Ethyl furfuracrylate, $\text{C}_4\text{H}_3\text{O}\cdot\text{CH}\cdot\text{CH}\cdot\text{COOEt}$, is prepared by heating furfuropropionic acid with an equal weight of alcohol and one-fourth its weight of sulphuric acid for four hours at 100° . It is a colourless oil of pleasant odour and bitter taste, boils at $228\text{--}230^\circ$ without decomposition, and is insoluble in water but miscible with alcohol and ether.

W. P. W.

Furfuralmalonic Acid. By W. MARCKWALD (*Ber.*, **21**, 1080—1083).—*Diethyl furfuralmalonate*, $\text{C}_4\text{H}_3\text{O}\cdot\text{CH}\cdot\text{C}(\text{COOEt})_2$, is obtained by heating a mixture of furfuraldehyde and ethyl malonate with acetic anhydride; the product is a slightly yellow, thick oil, with an ethereal odour and sharp bitter taste. It is insoluble in water, but mixes with alcohol and other solvents in all proportions.

Furfuralmalonic acid, $\text{C}_4\text{H}_3\text{O}\cdot\text{CH}\cdot\text{C}(\text{COOH})_2$, obtained by hydrolysing the ethyl salt, crystallises from ether, alcohol, or glacial acetic acid in compact prisms, which melt at 187° with decomposition, are readily soluble in water, but insoluble in benzene, light petroleum, and chloroform. When heated above its melting point, carbonic anhydride is evolved, and furfuracrylic acid is obtained. The salts are mostly readily soluble.

Monethyl furfuralmalonate, $\text{C}_4\text{H}_3\text{O}\cdot\text{CH}(\text{COOH})\cdot\text{COOEt}$, is formed by gently heating the diethyl salt for a short time with an excess of potash; it crystallises from benzene in large, thick, transparent, slightly yellow, rhombic prisms, melting at $102\cdot5^\circ$. It is very sparingly soluble in cold, more readily in hot water, dissolves tolerably readily in benzene and chloroform, but is insoluble in light petroleum. When distilled, it yields carbonic anhydride and ethyl furfuracrylate. The alkaline salts are readily, those of the alkaline earths and the heavy metals only sparingly, soluble.

Furfuralmalonamide, $\text{C}_4\text{H}_3\text{O}\cdot\text{CH}\cdot\text{C}(\text{COONH}_2)_2$, is obtained by the action of concentrated ammonia on diethyl furfuralmalonate. It is tolerably readily soluble in hot water and boiling alcohol, from which it crystallises in white needles, melting at 180° with decomposition; it dissolves very readily in glacial acetic acid, but is insoluble in ether,

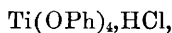
benzene, light petroleum, and chloroform. On boiling with hydrochloric acid, it yields ammonia and furfuralmalonic acid.

Furfurylmalonic acid, $C_4H_3O \cdot CH_2 \cdot CH(COOH)_2$, is formed when furfuralmalonic acid is reduced with sodium amalgam. It is readily soluble in water, ether, glacial acetic acid, and alcohol, from which it crystallises in long, slender, colourless needles, melting at 125° , but it is almost insoluble in light petroleum, benzene, and chloroform. When distilled, it gives carbonic anhydride and furfuropropionic acid. Most of the salts are soluble in water. F. S. K.

Hexahydropseudocumene and its Relation to Mononaphthene. By M. KONOVALOFF (*Chem. Centr.*, 1887, 1133, from *Zurn. russk. obšč.*, 1887, 255—257).—Pure *hexahydropseudocumene*, the product of the action of hydriodic acid and phosphorus on pseudocumene, boils at 135 — 138° , and has sp. gr. 0.7812 at 0° , and 0.7667 at 20° (water at $0^\circ = 1$). *Nononaphthene*, prepared by Markownikoff and Ogloblin, boils at 135 — 136° , and has a sp. gr. 0.7808 at 0° , and 0.7652 at 20° .

Both these compounds behave in the same way towards nitric acid, a small quantity of a crystalline compound showing the melting point of trinitrocumene being the only product. With bromine in presence of aluminium bromide, they both react in the same way with formation of tribromopseudocumene and resinous substances. J. W. L.

Action of Titanium Chloride on Phenol. By A. SCHUMANN (*Ber.*, 21, 1079—1080).—*Phenyl orthotitanate hydrochloride*,



is obtained by acting on phenol in anhydrous benzene solution with titanium chloride, and crystallising the product from benzene. It decomposes on exposure to moist air, and yields phenol, titanous acid, and hydrochloric acid when treated with water. F. S. K.

Nitrosnitroresorcinol. By C. DE LA HARPE and F. REVERDIN (*Ber.*, 21, 1405—1407).—*Nitrosnitroresorcinol*, $OH \cdot C_6H_2O(NO_2) \cdot NOH$ [$OH : NO_2 : O : N \cdot OH = 1 : 2 : 3 : 4$], is obtained by adding an excess of dilute sulphuric acid to a cooled mixture of nitroresorcinol (m. p. = 85°), aqueous soda (10 per cent.), and sodium nitrite in equimolecular proportions. It crystallises in brown needles, does not melt at 200° but decomposes with explosion when heated beyond this temperature, and is readily soluble in water, acids, and alkalis, sparingly soluble in alcohol, and insoluble in benzene, ether, and chloroform. On reduction with tin and hydrochloric acid, it yields a diamidoresorcinol identical with that obtained from dinitroresorcinol. When treated in aqueous solution with ferrous sulphate or iron filings, it gives an intense green coloration owing to the formation of a dye which can be separated by the addition of salt. This, in an acid bath, dyes wool green. A mixture of nitrosnitroresorcinol and resorcinol dissolves in concentrated sulphuric acid with a green colour, which gradually changes through blue to violet. W. P. W.

Ethereal Oil of Asarum Europaeum L. By A. S. F. PETERSEN (*Ber.*, **21**, 1057—1064).—The oil obtained from *Asarum europaeum* is a thick, dark-brown, neutral liquid with a sweet, aromatic odour; it dissolves readily in ordinary solvents, and on long exposure to winter cold deposits crystals of asarone in considerable quantities. The oil can be separated into two chief portions by distilling with steam and subsequent fractioning. The fraction boiling about 175° contains a terpene, which was found to be identical with pinene. The fraction boiling at 240—260°, on further fractioning, yields a slightly yellow oil which boils at 247—253°, and has the formula $C_{11}H_{14}O_2$.

The halogens act energetically on this compound, and when heated with concentrated hydriodic acid it yields methyl iodide in quantities which show the presence of two methoxy-groups. Nitrous acid converts it into a compound, $C_{11}H_{14}O_2N_2O_3$, which crystallises in slender yellow needles, melting at 118°, insoluble in water, but soluble in glacial acetic acid and dilute alcohol. When oxidised with nitric acid, the oil yields a resinous product, oxalic acid, and small quantities of an acid melting at 178°, considerable quantities of carbonic anhydride and hydrogen cyanide being evolved. By careful oxidation with potassium permanganate, acetic acid, oxalic acid, and veratric acid are obtained with evolution of a considerable quantity of carbonic anhydride.

The chief constituent of asarum oil is therefore a compound which has probably the constitution $C_6H_3(C_3H_5)(OMe)_2 [C_3H_5 : OMe : OMe = 1 : 3 : 4]$. The oil obtained from *Asarum canadense* L. also contains pinene, but differs from that of *Asarum europaeum*, inasmuch as considerable quantities of acetic acid are evolved when the oil is fractioned.

F. S. K.

Bromeugenol-derivatives. By E. v. BOYEN (*Ber.*, **21**, 1393—1397).—Dibromeugenol, obtained by the reduction of dibromeugenol dibromide in alcoholic solution with zinc-dust, dissolves readily in alkalis forming salts which crystallise in lustrous scales; the potassium, $C_3H_5 \cdot C_6HBr_2(OMe) \cdot OK$, sodium, and ammonium salts were prepared. The *acetyl*-derivative, $C_3H_5 \cdot C_6HBr_2(OMe) \cdot OAc$, crystallises from ether in large, colourless, hexagonal prisms, from alcohol in groups of silky prisms, and melts at 66°. Nitro-derivatives of dibromeugenol could not be obtained. The *methyl ether* is crystalline, has a low melting point, and on oxidation with chromic acid mixture or permanganate is converted into a *dibromodimethoxybenzoic acid*, $(OMe)_2 \cdot C_6HBr_2 \cdot COOH$. This crystallises from high boiling petroleum in slender, lustrous needles, from water in silvery scales, melts at 182°, and is sparingly soluble in water, soluble in alcohol, ether, and acetic acid. The *zinc* salt is characteristic, and forms radiating groups of silvery crystals, which are equally as soluble in cold as in hot water; the *silver* salt is crystalline, and decomposes on boiling with water.

Dibromeugenol dibromide does not form salts with alkalis, but yields amorphous products whose nature has not yet been determined. The *acetyl*-derivative, $C_3H_5Br_2 \cdot C_6HBr_2(OMe) \cdot OAc$, crystallises from

alcohol in slender prisms, from ether in rhombic tables, melts at 91° , and is soluble in benzene and acetic acid, readily soluble in ether. The *benzoyl*-derivative crystallises from light petroleum in tufts of needles, melts at 113° , and is sparingly soluble in alcohol and ether, soluble in benzene and acetic acid.

W. P. W.

Amidoisopropylbenzenes. By E. J. CONSTAM and H. GOLDSCHMIDT (*Ber.*, **21**, 1157—1162).—In order to compare Nicholson's cumidine (*Annalen*, **65**, 58) with the paramidoisopropylbenzene prepared by Louis (*Ber.*, **16**, 111), the authors have nitrated cumene from cumic acid with a mixture of nitric and sulphuric acids at the ordinary temperature, and reduced the nitro-derivative with zinc and hydrochloric acid. A mixture of two bases is obtained, and these can be partially separated by means of their oxalates, of which the less soluble melts at 157 — 158° , and the more soluble at 125 — 128° . The less soluble salt, on treatment with aqueous soda, yields a colourless oil, which rapidly becomes dark-coloured on exposure to light, has an aromatic odour, boils at 217 — 220° , and does not solidify at -20° . This amido-derivative can be converted into paraisopropylbenzoic acid, and is identical with Nicholson's compound. The *oxalate*, $(C_9H_{13}N)_2 \cdot H_2C_2O_4 + 2H_2O$, crystallises in white, silvery scales, melts at 159° with decomposition, and is very sparingly soluble in water; the *acetyl*-derivative, $C_9H_{11} \cdot NHAc$, crystallises in white, lustrous scales, and melts at 102 — 102.5° ; and the *carbamide*-derivative, $CHMe_2 \cdot C_6H_4 \cdot NH \cdot CONH_2$, crystallises in slender, colourless needles, and melts at 152° . The base obtained by Louis' method also yields paraisopropylbenzoic acid, and, contrary to his statement, yields a crystalline oxalate and acetyl-derivative which are identical with the compounds just described, consequently the bases obtained both by Nicholson and Louis have the constitution $[NH_2 : Pr = 1 : 4]$.

The more soluble oxalate (m. p. = 125 — 128°) is a mixture of the oxalates of ortho- and para-amidoisopropylbenzene, and can be separated into its constituents by treatment with aqueous soda and fractional crystallisation of the acetyl-derivatives of the two bases. Orthamidoisopropylbenzene boils at 213.5 — 214.5° at 732 mm. pressure, and does not solidify in a freezing mixture. The *hydrochloride*, $C_9H_{13}N \cdot HCl$, crystallises in large, colourless, seemingly rhombic prisms, which rapidly become opaque on exposure to the air; the *oxalate*, $(C_9H_{13}N)_2 \cdot H_2C_2O_4 + H_2O$, crystallises in long, colourless prisms and melts at 173° ; the *acetyl*-derivative, $C_9H_{11} \cdot NHAc$, crystallises in tufts of colourless needles and melts at 72° ; the *carbamide*-derivative, $CHMe_2 \cdot C_6H_4 \cdot NH \cdot CONH_2$, crystallises in small, white needles and melts at 133 — 134° .

W. P. W.

Compounds of Alloxan with Aromatic Amines. By G. PELLIZZARI (*Chem. Centr.*, 1887, 1288 and 1396, from *L'Orosi*, **10**, 253—263 and 295—302).—Alloxan gives additive compounds with aromatic bases in aqueous solution which are not salts, as the base cannot be separated from them.

α -Naphthylaminealloxan, $C_{14}H_{11}N_3O_4$, is insoluble in water, sparingly soluble in ether, light petroleum, and chloroform; from alcohol it

crystallises in slender, white needles. It is insoluble in acids and in ammonia, soluble in fixed alkalis, by which it is changed into a new acid, $C_{14}H_{10}N_2O_4$; this separates from dilute alcohol in long needles, is insoluble in ether, light petroleum, chloroform, readily so in alcohol and acetic acid. When boiled with alkali, the acid loses carbon dioxide and ammonia. β -Naphthylamine gives no additive product.

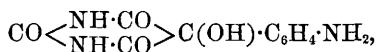
Anilalloxan, $C_{10}H_8N_3O_4$, crystallises from alcohol in needles which decompose at 248° . It is soluble in hot water. The compound behaves as an amido-acid, and forms salts both with alkalis and with acids. Fixed alkalis dissolve it with formation of a new acid, $C_6H_8N_2O_3$. This decomposes at 130° , crystallises from ethyl acetate in slender, white needles, is sparingly soluble in water and ether, readily so in alcohol; when boiled with alkalis, it loses carbonic anhydride and ammonia.

Orthotoluidinealloxan forms white needles which on heating decompose without melting. It has both acid and basic properties. With alkalis it forms a new acid. Paratoluidine does not react with alloxan.

Pseudocumindinealloxan forms a crystalline powder and yields a new acid when treated with alkalis.

Secondary bases form analogous alloxan compounds. *Methylanilalloxan*, $C_{11}H_{11}N_3O_4$, crystallises from water in white plates. The aqueous solution is decomposed by boiling. It yields salts with bases and with acids. Cold alkali solution decomposes it into carbonic anhydride, ammonia, and an acid which could not be obtained in a crystallised state. *Diphenylaminealloxan* separates from alcohol as a crystalline powder of feebly basic properties; with alkalis, it yields an acid. Tertiary bases also react with alloxan in the same way. *Dimethylanilalloxan* forms shining white crystals. It is very sparingly soluble in water, readily so in hot alcohol. It is more stable than anil- and methylanil-alloxan, and yields crystalline salts with acids.

Several salts of dimethylanilalloxan were prepared, amongst them the silver salt, $C_{12}H_{12}AgN_3O_4$. Dilute potash solution dissolves dimethylanilalloxan; acetic acid precipitates from this solution the compound $C_{10}H_{12}N_2O_3$. This crystallises from alcohol in needles, decomposing at 281° . It has acid properties. *Diethylanilalloxan* is prepared in a manner analogous to the dimethyl-compound, and has similar properties. The author concludes that the constitution of anilalloxan is expressed by the formula

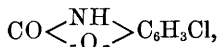


and that the other compounds have corresponding constitutions.

J. W. L.

Action of Chlorine on Carbonylorthamidophenol. By R. JACOBY (*J. pr. Chem.* [2], 37, 28—52).—Carbonylorthamidophenol, $CO < \begin{smallmatrix} NH \\ O \end{smallmatrix} > C_6H_4$, is best prepared by passing dry carbonyl chloride through dry benzene in which orthamidophenol is suspended, as long as a rise of temperature is observed. The residue obtained by evaporating the benzene is dissolved in water, treated with stannous chloride, boiled for a few minutes, and filtered. The nearly colourless

filtrate deposits slightly reddish plates of carbonylamidophenol. It boils above 360° . When heated with hydrochloric acid above 150° , it takes up 1 mol. H_2O , and decomposes into carbonic anhydride and amidophenol. When the aqueous solution in presence of hydrochloric acid is gradually treated with a solution of bleaching powder, a crystalline precipitate is formed, consisting probably of a mixture of two chlorimides, $\text{CO} < \begin{smallmatrix} \text{NCl} \\ \text{O} \end{smallmatrix} > \text{C}_6\text{H}_4$ and $\text{CO} < \begin{smallmatrix} \text{NCl} \\ \text{O} \end{smallmatrix} > \text{C}_6\text{H}_3\text{Cl}$. When this is boiled with alcohol, carbonylchloramidophenol,



separates in large prisms melting at $192\text{--}193^{\circ}$. The same chlorinated compound is also formed by the action of water and of aniline on the mixed chlorimides.

Carbonyltrichloramidophenol, $\text{CO} < \begin{smallmatrix} \text{NH} \\ \text{O} \end{smallmatrix} > \text{C}_6\text{HCl}_3$, is obtained by passing chlorine through a solution of carbonylamidophenol in cold glacial acetic acid, and boiling the mixed chlorimides so formed with alcohol. It crystallises in needles, melts at $261\text{--}262^{\circ}$, and sublimes without decomposition when carefully heated. It is almost insoluble in cold solvents. A small amount of a compound melting at $184\text{--}186^{\circ}$ is also formed in the reaction.

Carbonylchlorophenylchlorimide, $\text{CO} < \begin{smallmatrix} \text{NCl} \\ \text{O} \end{smallmatrix} > \text{C}_6\text{H}_3\text{Cl}$, is formed when a solution of bleaching powder is added to a solution of carbonylchloramidophenol in presence of hydrochloric acid. It melts at $119\text{--}120^{\circ}$. It is very readily soluble in ether, soluble in chloroform and benzene. Alcohol, water, aniline, and dimethylaniline decompose it, yielding carbonylchloramidophenol. When the dry chlorimide is heated, it melts, and directly afterwards explodes. When the substance is carefully heated in small quantities in a large flask, the decomposition takes place without violence, and the products can be collected. A compound was isolated, which was shown by analysis to be an isomeric dichloride.

α -*Carbonyldichloramidophenol*, $\text{CO} < \begin{smallmatrix} \text{NH} \\ \text{O} \end{smallmatrix} > \text{C}_6\text{H}_2\text{Cl}_2$, crystallises in sparingly soluble prisms melting at 270° ; when heated with hydrochloric acid at 200° , it takes up 1 mol. H_2O , and decomposes into dichloramidophenol and carbonic anhydride. The ammoniacal solution yields a silver salt when treated with silver nitrate.

β -*Carbonyldichloramidophenol* is contained in small amount in the more soluble portions of the product obtained by heating carbonylchlorophenylchlorimide. It crystallises in lustrous needles melting at $213\text{--}214^{\circ}$, very readily soluble in alcohol, ether, and glacial acetic acid, less soluble in water.

α -*Carbonyldichlorophenylchlorimide*, $\text{CO} < \begin{smallmatrix} \text{NCl} \\ \text{O} \end{smallmatrix} > \text{C}_6\text{H}_2\text{Cl}_2$, prepared by precipitating a solution of α -carbonyldichlorimidophenol in glacial acetic acid with a solution of bleaching powder, begins to melt at $145\text{--}150^{\circ}$ with decomposition. Boiling alcohol converts it quantita-

tively into carbonyldichlorophenol. It is very slowly decomposed by water. The β -compound forms white needles melting at about 89° . Cold alcohol decomposes it with evolution of chlorine. Both compounds explode when quickly heated.

Carbonyltrichlorophenolchlorimide, $C_7HCl_4NO_2$, crystallises in white needles, which begin to decompose above 130° , and detonate when heated quickly. Boiling water and boiling alcohol convert it quantitatively into carbonyltrichlorophenol.

Carbonyltetrachloramidophenol, $C_7HCl_4NO_2$, is obtained by carefully exploding small amounts of the chlorimide in a capacious flask. It melts at 220 – 237° , is soluble in alcohol, ether, and benzene, less soluble in water; it could not be obtained quite pure. Bleaching powder precipitates *carbonyltetrachlorophenolchlorimide* from the solution in glacial acetic acid.

Carbonylbromamidophenol (m. p. 186 – 187°) when treated with chlorine water, yields a *chlorimide*, $C_7H_3ClBrNO_2$, which melts at 118 – 120° and resembles the other chlorimides.

Carbonyldibromamidophenol, $C_7H_3Br_2NO_2$, obtained by the action of an excess of bromine-water on carbonylamidophenol, crystallises from alcohol in plates which melt at 243 – 245° with partial decomposition. It is insoluble in cold water. The *silver salt* forms white needles. The *chlorimide*, $C_7H_2Br_2ClNO_2$, crystallises in large needles melting at 120° .
N. H. M.

Secondary Diamines containing an Ethylene-group. By A. COLSON (*Bull. Soc. Chim.*, **48**, 799–802; compare this vol., p. 139).—*Ethylene orthoditolylidiamine*, $C_8H_4(C_6H_5N)_2$, is prepared by heating a mixture of orthotoluidine and ethylene bromide. It is crystalline, dissolves in ether (7 parts), cold alcohol (10 to 12 parts), and boiling water (300 parts). The alcoholic solution (not the aqueous) reacts with acidified methyl-orange. The *hydrobromide* forms white crystals soluble in 30 parts of boiling water; the *hydrochloride* is sparingly soluble.
N. H. M.

Action of Nitrous Acid on some Organic Bases. **Dinitrosobenzenylamidine.** By W. LOSSEN and F. MIERAU (*Ber.*, **21**, 1250–1256).—*Benzenylamidine nitrite*, $NH_2 \cdot CPh \cdot NH \cdot HNO_2 + H_2O$, is obtained by evaporating a neutral solution of benzenylamidine hydrochloride with sodium nitrite. It forms well-defined plates which lose their water of crystallisation, and are gradually decomposed at 64° ; heated at a higher temperature, it yields benzonitrile, nitrogen, and water. It is readily soluble in water and alcohol, but insoluble in ether; it shows all the properties of a nitrite.

Dinitrosobenzenylamidinebenzenylamidine, $C_{14}H_{14}N_6O_2$, is formed by the action of nitrous acid on benzenylamidine in an acid solution. It crystallises in leaves which are sparingly soluble in cold water or alcohol, more readily in hot water, very readily in hot alcohol, but almost insoluble in ether. It explodes when heated at 178° , and is decomposed by an excess of acid with evolution of gas.

Potassium dinitrosobenzenylamidine, $C_7H_5KN_2(NO)_2$, is obtained by adding potash to a hot alcoholic solution of the preceding compound.

It crystallises in needles which are readily soluble in water, sparingly in alcohol, and insoluble in ether. In the dry state, the salt is very explosive, but in aqueous solution can be boiled without any decomposition taking place. An aqueous solution gives precipitates with barium chloride, lead acetate, and mercurous nitrate; ammonia, hydroxylamine hydrochloride, and methylaniline hydrochloride throw down precipitates of slender, colourless needles. The metallic precipitates are explosive in the dry state. An aqueous magenta solution produces a voluminous, dark-red precipitate.

Silver dinitrosobenzylamidine, $C_7H_5Ag(NO)_2N_2$, is also very explosive. F. S. K.

Mixed Diazo-compounds. By H. GOLDSCHMIDT and J. HOLM (*Ber.*, 21, 1016—1026).—*Diazobenzenebenzylamine*, $PhN_2 \cdot NH \cdot CH_2Ph$, is formed by the action of diazobenzene chloride on benzylamine; it crystallises from hot light petroleum in pale-yellow, thin, transparent leaves, melting at 72° , and is readily soluble in ether, benzene, and alcohol. This compound, like its higher homologues, is very readily acted on by acids; when boiled with hydrochloric acid, it behaves like a mixture of diazobenzenebenzylamine and diazobenzylaniline.

Paradiazotoluenebenzylamine, $C_6H_4Me \cdot N_2 \cdot NH \cdot CH_2Ph$, is obtained by the action of paradiazotoluene chloride on benzylamine; it forms slightly yellowish leaves melting at 77° , and is readily soluble in benzene, alcohol, and ether. When boiled with hydrochloric acid, it reacts like a mixture of diazobenzyltoluidine with a smaller quantity of diazotoluenebenzylamine.

Orthodiazotoluenebenzylamine is obtained in the form of a dark-yellow oil by the action of orthodiazotoluene chloride on benzylamine.

β -*Diazonaphthalenebenzylamine*, $C_{10}H_7 \cdot N_2 \cdot NH \cdot CH_2Ph$, is produced by the action of β -diazonaphthalene chloride on benzylamine; it separates from ether and benzene in brownish crystals melting at 110° .

New Method for Determining the Constitution of Mixed Diazoamido-compounds.—When the reaction product of diazobenzene chloride and benzylamine is dissolved in benzene, warmed for a few minutes with 1 mol. of phenyl isocyanate, and the benzene evaporated in a vacuum, a product is obtained which crystallises from alcohol in long, slender, snow-white needles melting at 119° . Analysis showed that this compound consists of 1 mol. of phenyl isocyanate in combination with 1 mol. of the diazoamido-compound. Two formulæ are possible for this substance, $NHPh \cdot CO \cdot N(CH_2Ph)N_2Ph$ and



When boiled with hydrochloric acid, it yields benzylphenylcarbamide, phenol, and a small quantity of benzyl chloride, which shows that the first formula is the correct one. The diazoamido-compound is therefore *diazobenzenebenzylamine*.

Similarly, the condensation-product of paradiazotoluene chloride and benzylamine yields with phenyl isocyanate a compound $C_{21}H_{20}N_4O$, which crystallises from alcohol in slender, white needles melting at 115 — 116° . By boiling this substance with hydrochloric acid, benzyl-

phenylcarbamide, paracresol, and a small quantity of benzyl chloride are obtained, showing that the diazoamido-compound is *paradiazotoluenebenzylamine*. From these experiments, it follows that the reaction between diazochlorides and benzylamine is normal.

Dis-paradiazotoluene-ethylamine, $\text{N}\ddot{\text{E}}\text{t}(\text{N}_2\cdot\text{C}_6\text{H}_4\text{Me})_2$, is formed by the action of paradiazotoluene chloride on ethylamine. It crystallises from ether in bright-yellow, transparent needles which melt at 121° with copious evolution of gas; it is readily soluble in ether, benzene, and hot light petroleum, sparingly in ether and cold light petroleum. When boiled with dilute sulphuric acid, it yields paratoluidine, paracresol, ethylamine, ethyl alcohol, and nitrogen. F. S. K.

Substitution-products of Parazotoluene. By J. V. JANOVSKY and K. REIMANN (*Ber.*, **21**, 1213—1219; compare Abstr., 1887, 479).—Three substitution-products are obtained by the action of bromine on parazotoluene in glacial acetic acid solution.

Orthobromazotoluene, $\text{C}_6\text{H}_3\text{MeBr}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Me}$, separates from the glacial acetic acid solution and, after recrystallising from alcohol, is obtained in golden-orange-coloured, rhombic plates melting at 139° .

Bromazotoluenesulphonic acid, $\text{C}_6\text{H}_3\text{MeBr}\cdot\text{N}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{SO}_3\text{H} + 1\frac{1}{2}\text{H}_2\text{O}$, is formed by acting on the preceding compound with sulphuric acid containing sulphuric anhydride. It yields very characteristic salts which are mostly sparingly soluble in water. The *potassium* salt, $\text{C}_{14}\text{H}_{12}\text{BrN}_2\cdot\text{SO}_3\text{K}$, crystallises in rhombic prisms. The *sodium* salt forms large, anhydrous, shining, golden prisms. The *copper* and *cadmium* salts are yellow, crystalline compounds. Paratoluidine, orthosulphonic acid and metabromoparatoluidine are obtained when the acid is treated with tin and hydrochloric acid.

Metabromazotoluene remains in the mother-liquor from the ortho-compound, and is precipitated on adding water. It crystallises from alcohol in small, orange-yellow leaflets which are readily soluble in ether, acetone, and benzene, and melt at 128° . When treated with alcoholic ammonia and hydrogen sulphide, a hydrazobromotoluene, melting at 113° , is obtained. It yields a sulphonic acid, the sodium, potassium, and copper salts of which are readily soluble, and the acid, when reduced with tin and hydrochloric acid, gives paratoluidine, meta-sulphonic acid $[\text{Me} : \text{SO}_3\text{H} : \text{NH}_2 = 1 : 3 : 4]$ and orthobromoparatoluidine $[\text{Me} : \text{Br} : \text{NH}_2 = 1 : 2 : 4]$, melting at $20\text{--}23^\circ$.

The bromazotoluenesulphonic acid previously described (*loc. cit.*) must have the constitution $[\text{Me} : \text{Br} : \text{N}_2 : \text{SO}_3\text{H} : \text{Me} = 4 : 3 : 1 : 3 : 4]$.

Dimetadibromazotoluene, $\text{N}_2(\text{C}_6\text{H}_3\text{BrMe})_2$ $[\text{Me} : \text{Br} : \text{N} = 1 : 2 : 4]$, is contained in the mother-liquor from the metabromazotoluene. It is a yellow, crystalline compound melting at 75° . When reduced, it yields orthobromotoluidine melting at 25° . F. S. K.

Action of Carbonyl Chloride on Hydrazides. By M. FREUND and B. B. GOLDSMITH (*Ber.*, **21**, 1240—1244).—*Malonyl hydrazide*, $\text{CH}_2(\text{CO}\cdot\text{NH}\cdot\text{NHPh})_2$, obtained by heating ethyl malonate or malonamide with phenylhydrazine, crystallises from dilute alcohol in white

leaflets which melt at 187° , are insoluble in water, but dissolve readily in alcohol, chloroform, and glacial acetic acid. When heated with a benzene solution of carbonyl chloride, a compound, $C_{17}H_{12}N_4O_4$, is obtained which crystallises from glacial acetic acid in yellowish-coloured leaves melting at 205° ; it is very sparingly soluble in water and alcohol, and only sparingly soluble in benzene.

Ethylmalonyl hydrazide, $CH_3Et(CO\cdot NH\cdot NHPh)_2$, prepared by heating ethylmalonamide with phenylhydrazine, crystallises from glacial acetic acid in white needles which melt at 233° ; it is sparingly soluble in alcohol and insoluble in water. When treated with carbonyl chloride, it yields a compound, $C_{19}H_{16}N_4O_4$, which crystallises from glacial acetic acid or alcohol, and melts at $112-113^{\circ}$.

Oxalyl hydrazide and carbonyl chloride give a product, $C_{16}H_{10}N_4O_4$, which is not acted on by alkalis or concentrated hydrochloric acid, and crystallises in microscopic forms melting above 300° .

Acetyl hydrazide and carbonyl chloride yield a compound, $C_{16}H_{16}N_4O_4$, which crystallises from dilute alcohol in white prisms. It melts at $93-94^{\circ}$, and can be distilled without decomposition.

F. S. K.

Action of Carbamide on Hydrazines. By A. PINNER (*Ber.*, 21, 1219—1227; compare Abstr., 1887, 1042; also Skinner and Ruhemann, this vol., p. 274).—Phenylurazole is formed by heating phenylsemicarbazide with carbamide (2 mols.) at $150-160^{\circ}$; also by heating a mixture of phenylhydrazine hydrochloride and biuret suspended in amyl alcohol.

Orthotolylsemicarbazide, $C_8H_{11}N_3O$, is produced when orthotolylhydrazine is heated with carbamide (2 mols.). It crystallises in flat, compact needles melting at $159-160^{\circ}$, is tolerably readily soluble in water, sparingly in alcohol, and insoluble in ether and benzene. It reduces Fehling's and ammoniacal silver solution.

Orthotolylurazole, $C_8H_9N_3O_2$, is obtained by heating tolylhydrazine hydrochloride with carbamide (4 mols.). It forms white leaflets which melt at 170° and dissolve readily in hot, tolerably readily in cold water. It dissolves in dilute alkalis and ammonia, forming reddish solutions.

Paratolylsemicarbazide crystallises in shining leaves melting at $157-158^{\circ}$. It is only sparingly soluble in cold water, but dissolves rather easily in alcohol and hot water. It reduces ammoniacal silver and alkaline copper solutions.

Paratolylurazole crystallises in slender, yellowish needles which melt at 274° with decomposition. It is very sparingly soluble in both hot and cold water.

α -*Naphthylsemicarbazide*, $C_{10}H_7NH\cdot NH\cdot CONH_2$, is formed when α -naphthylhydrazine hydrochloride and carbamide are heated together at 140° . It crystallises from boiling amyl alcohol in thin, shining, slightly brownish leaves which melt at 231° and are insoluble in water and ether. It is sparingly soluble in alcohol, benzene, ammonia, and dilute alkalis, and reduces Fehling's solution.

β -*Naphthylsemicarbazide* forms thin leaves which melt at 225° and towards solvents behaves like the α -compound.

Nitrous acid has no action on phenylurazole; bromine and phosphorous pentachloride react only at a high temperature causing complete decomposition.

Dimethylphenylurazole, $C_8H_5Me_2N_3O_2$, was obtained in an impure state by heating the urazole with potash, methyl iodide, and a small quantity of methyl alcohol. It crystallises in white needles melting at 90° .

The *acetyl*-derivative, $C_8H_5Ac_2N_3O_2$, crystallises from benzene in white needles which melt at 141 — 149° , and are insoluble in water.

When phenylsemicarbazide is heated at 160 — 170° for four to five hours, ammonia, carbonic anhydride, carbon monoxide, and benzene are evolved and a brownish, vitreous mass remains. This residue consists chiefly of unchanged semicarbazide mixed with a considerable quantity of phenylurazole, but it also contains a new compound which remains behind in the form of a white, crystalline, granular mass when the residue is extracted with boiling water. This compound has the empirical formula $C_7H_6N_2O$; it melts at almost the same temperature as phenylurazole (264°) and, like the latter, dissolves readily in alkalis and ammonia; it is, however, very sparingly soluble in hot water, hot alcohol, and other solvents. It dissolves in ammonia without change, but when precipitated from its solution in soda it melts at 231° .
F. S. K.

Phenosafranine. By P. BARBIER and L. VIGNON (*Bull. Soc. Chim.*, **48**, 338—342).—When a mixture of paraphenylenediamine and aniline (eq. mols.) is oxidised at a low temperature, a blue compound is obtained which changes gradually at the ordinary temperatures, instantly at 100° , into phenosafranine. Owing to its instability, the blue compound could not be analysed, but its conversion into phenosafranine is shown to take place without addition or elimination of any substance. It is converted by the action of zinc and hydrochloric acid at a low temperature into aniline and a new *leuco-base* which,

when exposed to air, yields *amidophenazine*, $C_6H_4 \begin{array}{c} \diagup N \diagdown \\ | \\ N \end{array} C_6H_3 \cdot NH_2$,

the *hydrochloride* of which crystallises in slender, violet-red needles. When this is reduced with zinc and hydrochloric acid, the leuco-base, $C_6H_4 \begin{array}{c} \diagup NH \diagdown \\ | \\ NH \end{array} C_6H_3 \cdot NH_2$, is obtained. By oxidising this leuco-base in presence of aniline at a low temperature, the blue compound is regenerated.

The constitutional formulæ, $N \begin{array}{c} \diagup C_6H_3(NH_2) \diagdown \\ | \\ C_6H_4 \end{array} NCl \cdot C_6H_4 \cdot NH_2$ and $N \begin{array}{c} \diagup C_6H_3(NH_2) \diagdown \\ | \\ C_6H_4 \end{array} NCl \cdot NHPh$, are ascribed to safranine and to the blue compound respectively.
N. H. M.

Alkylformanilides. By A. PICTET and P. CRÉPIEUX (*Ber.*, **21**, 1106—1111).—Alkylformanilides can readily be prepared by dissolv-

ing formanilide (1 mol.) in a small quantity of alcohol, adding the alkyl bromide (1 mol.), and finally an alcoholic solution of potassium hydroxide (1 mol.); the reaction takes place either in the cold or on gently warming. The method devised by Norton and Livermore (Abstr., 1887, 1038) for the preparation of methylformanilide cannot be employed for the preparation of its homologues, since sodium formanilide does not react either with ethyl bromide or with isopropyl bromide. The alkylformanilides are colourless, odourless, strongly refractive liquids, which do not solidify in a freezing mixture, boil at the same temperatures as the corresponding alkylacetanilides, and are insoluble in water, sparingly soluble in light petroleum, and readily soluble in the usual solvents. On distillation, they decompose slightly with formation on the one hand of carbonic oxide and the corresponding alkyaniline, and on the other of alcohol and benzonitrile or phenylcarbamine; when heated at 100° with alcoholic potash or concentrated hydrochloric acid, they are readily converted into the corresponding alkyanilines.

Methylformanilide boils at 253° under 716 mm. pressure, and has a sp. gr. = 1.097 at 18° ; it could not, however, be solidified by prolonged cooling in a freezing mixture (compare Norton and Livermore, *loc. cit.*). The methylaniline and methylacetanilide obtained from it boiled at 191° and 253° respectively under 712 mm. pressure. Ethylformanilide boils at 258° under 728 mm. pressure, and has a sp. gr. = 1.063 at 16° ; the corresponding ethylaniline boils at 203.5° under 712 mm. pressure and ethylacetanilide at 258° under 731 mm. pressure. Normal propylformanilide boils at 267° under 731 mm. pressure, and has a sp. gr. = 1.044 at 16° . The propylaniline derived from it boils at 219.5° at 716 mm. pressure, has a sp. gr. = 0.949 at 18° , and yields a nitrosamine which does not solidify in a freezing mixture (compare Döbner and v. Miller, Abstr., 1884, 1375); its acetyl-derivative boils at 266° under 712 mm. pressure, and crystallises from light petroleum or ether in large hexagonal scales melting at $47-48^{\circ}$. Isopropylformanilide boils at $261-263^{\circ}$ under 720 mm. pressure. The corresponding isopropylaniline is a colourless liquid, which boils at $209-210^{\circ}$ under 712 mm. pressure, and forms an oily nitrosamine and a platinumchloride crystallising in thick, yellowish-red prisms; its acetyl-derivative boils at $262-263^{\circ}$ under 712 mm. pressure, and crystallises from light petroleum in large, transparent tables having a camphor-like odour and melting at 39° . Isobutylformanilide boils at 274° under 731 mm. pressure. The isobutylaniline derived from it boils at $229-230^{\circ}$ under 716 mm. pressure, and has a sp. gr. = 0.94 at 18° ; its acetyl-derivative boils at $272-273^{\circ}$ under 712 mm. pressure, and does not solidify in a freezing mixture. Isoamylformanilide does not solidify at -12° , boils at $285-286^{\circ}$ under 728 mm. pressure, and has a sp. gr. = 1.004 at 16° . The corresponding isoamylaniline boils at 252.5° under 730 mm., and at 244.5° (uncorr.) under 712 mm. pressure, has a sp. gr. = 0.928 at 15° , and yields an acetyl-derivative boiling at 287° under 730 mm. pressure. Benzylformanilide decomposes on distillation into carbonic oxide and benzyaniline. The determinations of the boiling points were made with the thermometer immersed

in the vapour, and the specific gravity determinations are referred to the density of water at 4°.

Acetanilide boils at 301.5° (corr.) under 725 mm. pressure.

W. P. W.

Benzoylaldehyde. By L. CLAISEN and L. FISCHER (*Ber.*, **21**, 1135—1140; compare *Abstr.*, 1887, 940).—When an ethereal solution of benzoylaldehyde is treated with a solution of ammonium acetate in acetic acid, a derivative, $C_{18}H_{15}NO_2$, is obtained, which crystallises in bright-yellow, hair-like needles, melts at 219—220°, and is sparingly soluble in all the ordinary solvents. The *methylanilide* of benzoylaldehyde, $C_9H_7O \cdot NMePh$, forms compact white crystals melting at 103°, and the *benzylanilide*, $C_9H_7O \cdot NPhC_6H_5$, forms yellowish-white crystals, and melts at 130°. The *benzeneazo*-derivative,



crystallises in yellowish-red prisms, and melts at 103°. When treated with phenylhydrazine, benzoylaldehyde yields a white, crystalline *phenylhydrazone*, $CH_2Bz \cdot CH : N_2HPh$, melting at 118—120°, which on distillation yields a diphenylpyrazole identical with that prepared by Beyer and Claisen (*Abstr.*, 1887, 944).

The authors have failed to obtain the acetal of benzoylaldehyde by heating a mixture of ethyl orthoformate and acetophenone either alone or with acetic anhydride, but find that it reacts with acetic chloride even in the cold with the formation of triphenylbenzene. The reaction is in some way dependent on the presence of these three compounds, since triphenylbenzene is not formed when acetophenone is treated with acetic chloride, with ethyl orthoformate, or with a mixture of ethyl formate and acetic chloride.

W. P. W.

Benzenetriphenazine. By NIETZKI and A. W. SCHMIDT (*Ber.*, **21**, 1227—1230; compare Nietzki and Kehrmann, *Abstr.*, 1887, 473).—

Dihydroxyquinonephenazine, $CH_4 \begin{array}{c} \diagup N \diagdown \\ | \\ \diagdown N \diagup \end{array} C_6(OH)_2O_2$ [$OH : O : O : OH =$

1 : 2 : 3 : 4], is produced when a solution of sodium rhodizonate in dilute hydrochloric acid is mixed with an equivalent quantity of an orthophenylenediamine salt. It forms reddish-brown needles, which dissolve in dilute alkalis with a violet colour, but are sparingly soluble in acetic acid and indifferent solvents.

Diquinoylphenazine, $C_6H_4 \begin{array}{c} \diagup N \diagdown \\ | \\ \diagdown N \diagup \end{array} C_6O_4$, is formed by the action of

oxidising agents, such as dilute nitric acid, ferric chloride, &c., on the preceding compound. It exists only as the hydrate, and when dried at 100° has the composition $C_{12}H_4N_2O_4 \cdot 3H_2O$; it forms slightly yellowish needles, which are only sparingly soluble in water and acetic acid. It is decomposed when boiled with water, and is converted into dihydroxyquinonephenazine when treated with sulphurous acid.

Benzenetriphenazine, $C_6(N_2C_6H_4)_3$, is obtained by warming diquinoyl-

phenazine (1 mol.) with a dilute, aqueous solution of orthophenylenediamine sulphate (2 mols.). It is only sparingly soluble in most solvents, but dissolves rather easily in hot aniline; this solution on cooling deposits reddish-brown needles, which consist of benzene-triphenazine in loose combination with aniline. On washing with alcohol or water, these crystals are resolved into their constituents. When the compound is dissolved in glacial acetic acid and a few drops of concentrated hydrochloric acid added, an orange-red salt is precipitated, but dissolves again on boiling. The solution, on cooling, deposits triphenazine in greenish-yellow needles which do not melt, but sublime partially without decomposition at a high temperature. It is a very feeble base, and combines only with very concentrated acids to form orange-yellow salts which are decomposed by water.

Orthophenylenediamine sulphonic acid and rhodizonic acid yield a *monazine*, $C_{12}H_8N_2O_4 \cdot HSO_3$, crystallising in brownish-yellow needles which are soluble in hot water. F. S. K.

Action of Ethyl Oxalate on Acetophenone. By E. BRÖMME and L. CLAISEN (*Ber.*, 21, 1131—1135).—When treated with aqueous alkalis, ethyl benzoylpyruvate decomposes for the most part into acetophenone, ethyl alcohol, and the corresponding oxalate (*Abstr.*, 1887, 944), and a like decomposition occurs, although to a less extent, when a solution of potassium hydroxide in absolute alcohol is employed to effect the saponification. A good yield of benzoylpyruvic acid can, however, be obtained without the intermediate formation of the ethyl salt by adding a mixture of ethyl oxalate and acetophenone in molecular proportion to a warm alcoholic solution of sodium (2 at. props.), heating for half an hour, and after removal of the alcohol by distillation, treating the product with water. The solution of the sodium salt is then freed from any ethyl benzoylpyruvate or oxalyldiacetophenone by acidification with acetic acid, and the acid finally precipitated by the addition of hydrochloric acid. The authors consider it probable that the action of the acetophenone on the unstable double compound of ethyl oxalate with sodium ethoxide, $ONa \cdot C(OEt)_2 \cdot C(OEt)_2 \cdot ONa$, results in the formation of the compound $CHBz \cdot C(ONa) \cdot C(OEt)_2 \cdot CNa$, which on treatment with water yields ethyl alcohol and disodium benzoylpyruvate. Benzoylpyruvic acid crystallises with 1 mol. H_2O in short, white prisms, melts at 156—158° with the evolution of carbonic anhydride, and is readily soluble in methyl and ethyl alcohol, sparingly soluble in benzene and water. It is a strong acid, and forms with alkalis both normal and basic salts, the first of which are comparatively stable, whilst the latter when boiled with water decompose into acetophenone and the corresponding oxalate. Ferrous sulphate gives with dilute solutions of the sodium salt an evanescent, dark violet-red coloration, or with more concentrated solutions a dark-blue precipitate, which rapidly becomes greyish-blue, and finally brown; the *mercury* salt crystallising in colourless, lustrous, slender prisms is also characteristic. The *aniline*-derivative, $CH_3Bz \cdot C(NPh) \cdot COOH$, crystallises in citron-yellow prisms, and melts at 168—170° with decomposition.

Oxalyldiacetophenone, $\text{CH}_2\text{Bz}\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_2\text{Bz}$, is best obtained by adding to a mixture of anhydrous ether and sodium ethoxide (2 mols.) free from alcohol and cooled at 0° , first acetophenone (2 mols.) and then ethyl oxalate (1 mol.), and allowing the product to remain for several days; the resulting yellow salt is then dissolved in water, and decomposed by treatment with acetic acid. It crystallises from chloroform or acetic acid in lustrous, long, yellow prisms, melts at $179\text{--}180^\circ$, and is sparingly soluble in alcohol, ether, benzene, and light petroleum. Alkalis dissolve it with a yellow colour, and its solutions give a dark brownish-red coloration with alcoholic ferric chloride.

W. P. W.

Benzoylacetone. By L. CLAISEN and O. LOWMAN (*Ber.*, 21, 1149—1157).—When the sodium salt of benzoylacetone is treated with hydroxylamine, a crystalline compound is obtained, which melts at $67\text{--}68^\circ$, and has all the properties of the compound described as an oxime by Ceresole (*Abstr.*, 1884, 1167). On analysis, however, its composition is found to be $\text{C}_{10}\text{H}_9\text{ON}$, and on account of its great stability the authors ascribe to it the formula $\text{CPh}\cdot\text{N} - \text{CH}\cdot\text{CMe} > \text{O}$, regarding it as a derivative of a new class of compounds, the monazoles.

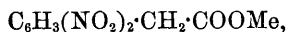
Homologues of benzoylacetone of the type $\text{CHR}\cdot\text{Ac}\cdot\text{Bz}$ could not be obtained by prolonged digestion of sodium benzoylacetone with ethyl iodide and alcohol on a water-bath; whilst treatment of the ketone, first with alcoholic potassium ethoxide, and then with ethyl iodide, results in the formation of ethyl benzoate and ethylacetophenone. *Ethyl benzoylacetone*, $\text{C}_{12}\text{H}_{14}\text{O}_2$, can, however, be prepared by heating a solution of benzoylacetone in benzene with the equivalent quantity of sodium wire until the whole is converted into the sodium-derivative of the ketone, and then digesting the product with ethyl iodide; it is a colourless oil boiling at $265\text{--}270^\circ$.

Contrary to expectation, the authors find that acetic chloride does not react with the sodium-derivative of dibenzoylmethane, and in view of the fact that Fischer and Bülow's dibenzoylacetone is not further acted on by sodium in boiling toluene (*Abstr.*, 1885, 1237), and that tribenzoylmethane does not yield a tetrabenzoyl-derivative when treated with sodium ethoxide and benzoic chloride, they suggest that the sodium-derivatives of diketones may have the formula $\text{R}\cdot\text{CO}\cdot\text{CH}\cdot\text{C}(\text{ONa})\text{R}'$. Further experiments are promised.

The remainder of the paper is devoted to a discussion of the theory of the formation of ethyl acetoacetate advocated by the authors (*Abstr.*, 1887, 584, 944; compare also Armstrong, *Proc.*, 1887, 79), and it is pointed out that the failure to obtain a condensation compound by the action of ethyl isobutyrate on ethyl oxalate in the presence of sodium (Wislicenus, *Ber.*, 20, 3396), affords confirmatory evidence in favour of the theory, since ethyl oxalate cannot yield derivatives with secondary acids if the reaction proceeds, as the authors suppose, according to the equation $\text{COOEt}\cdot\text{C}(\text{ONa})(\text{OEt})_2 + \text{CH}_2\text{R}\cdot\text{COOEt} = \text{COOEt}\cdot\text{C}(\text{ONa})\cdot\text{CR}\cdot\text{COOEt} + 2\text{EtOH}$.

W. P. W.

Phenylacetic Acid and Benzyl Cyanide. By A. MEYER (*Ber.*, 21, 1306—1316).—*Methyl dinitrophenylacetate*,



crystallises from alcohol in long, yellowish needles, melting at 82°.

Methyl azobenzenedinitrophenylacetate,



is prepared by dissolving methyl dinitrophenylacetate (1 gram) in alcohol (25 grams), adding a solution of sodium acetate (5 grams) in a little water, and carefully treating the whole with a solution of the calculated amount of diazobenzene chloride. It crystallises from alcohol in golden-yellow needles, melting at 182°.

Benzylbenzyl cyanide, $\text{CH}_2\text{Ph}\cdot\text{CHPh}\cdot\text{CN}$, is obtained by treating benzyl cyanide with sodium dissolved in 10 parts of absolute alcohol; and after half an hour the product is heated for some hours at 120° with benzyl chloride. The whole is then treated with water, extracted with ether, and the oil obtained by evaporating the ether distilled; it crystallises from dilute alcohol in white needles readily soluble in ether, melts at 58°, and boils without decomposition at about 335°. Phenylacetamide (which melts at 156° and boils at 280° to 300°, not 181—184°, Weddige, *J. pr. Chem.* [2], 7, 100), and the compound, $\text{CH}_2\text{Ph}\cdot\text{CHPh}\cdot\text{C}(\text{NH}\cdot\text{C}_7\text{H}_7):\text{NH}$, are also formed in the reaction. The latter crystallises from glacial acetic acid in white needles of a silky lustre melting at 182°.

Benzylphenylacetic acid, $\text{CH}_2\text{Ph}\cdot\text{CHPh}\cdot\text{COOH}$, is prepared by boiling benzylbenzyl cyanide with a slight excess of alcoholic potash for 1½ days. It dissolves readily in dilute alcohol and ether, and in much hot water, from which it crystallises in lustrous needles which melt at 91° and boil at 330—340°. The *silver salt* is an insoluble powder. The *calcium salt* with 1 mol. H_2O crystallises in white needles readily soluble in hot water and in alcohol. The *barium* and *zinc salts* are described. The *methyl salt* crystallises in needles melting at 34°; the *ethyl* and *propyl salts* are oils, and boil at 325° and 338—339° respectively. The *amide* crystallises in needles which melt at 133—134°, and dissolve readily in alcohol and ether.

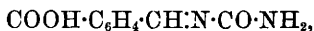
Isonitrosobenzyl cyanide, $\text{CN}\cdot\text{CPh}\cdot\text{N}\cdot\text{OH}$, is formed when a cooled alcoholic solution of sodium ethoxide and benzyl cyanide is saturated with nitrous acid. It crystallises from water in white plates which melt at 129°, and dissolve readily in alcohol, ether, and hot alcohol. The *silver salt*, $\text{CN}\cdot\text{CPh}\cdot\text{N}\cdot\text{OAg}$, forms sparingly soluble yellow crystals. When the cyanide is saponified, isonitrosophenylacetic acid (m. p. 127—128°, Müller, *Abstr.*, 1884, 1129) is obtained.

Benzylphenylacetic acid has the same constitution as Wurtz's dibenzylcarboxylic acid (*Annalen*, Suppl. 8, 51) and Ogliadoro's phenylhydrocinnamic acid (*Abstr.*, 1879, 641), to which lower melting points are ascribed.

N. H. M.

Derivatives of Orthophthalaldehydic Acid. By S. RACINE (*Compt. rend.*, 106, 947—949).—With carbamide, orthophthalaldehydic

acid readily forms a ureide which is deposited in slender needles even from very dilute solutions. It has the composition



and is insoluble in cold water, alcohol, or ether, but dissolves readily in boiling water, and to a slight extent in boiling alcohol. It is easily soluble in alkaline hydroxides and carbonates, and when heated with sodium hydroxide it evolves ammonia. It melts at 240° with evolution of ammonia and formation of a yellow substance which has not yet been examined. The silver salt is readily soluble in boiling water from which it separates in slender needles. The barium and calcium salts are almost insoluble in water whether hot or cold. No dibromide was obtained by the action of bromine on the ureide. When the sodium salt is mixed with hydroxylamine hydrochloride, it yields benzaldoximo-orthocarboxylic acid (Abstr., 1887, 951).

When dibromophthalide and anhydrous sodium acetate are heated together, a neutral substance is obtained similar in all its properties to the substance which is formed by the action of acetic anhydride on the orthophthalaldehydic acid (*loc. cit.*). C. H. B.

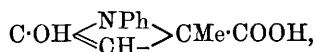
Derivatives of Phenylparacoumaric and Methylatropic Acids.

By A. CABELLA (*Chem. Centr.*, 1888, 34, from *Rendi. Accad. Nap.* [2], 1, 220—224).—Silver phenylparacoumarate, $\text{C}_{15}\text{H}_{11}\text{O}_3\text{Ag}$, is almost insoluble in water, and very stable. The methyl salt was obtained by passing dry hydrogen chloride through a solution of the acid in methyl alcohol, evaporating and crystallising the residue from weak alcohol; it forms white plates melting at 168 — 170° . The ethyl salt, $\text{C}_{17}\text{H}_{15}\text{O}_3$, melts at 151 — 152° , and is obtained by heating the silver salt of the acid with ethyl iodide at 110° .

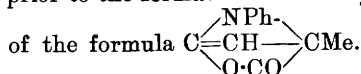
Silver methylatropate, $\text{C}_{10}\text{H}_9\text{O}_2\text{Ag}$, is moderately soluble in hot water, but unstable. J. P. L.

Condensation Products from β -Anilido-acids. By A. REISSERT (*Ber.*, 21, 1362—1391; compare Abstr., 1885, 900; 1886, 551).—Anilidopyrotartaric acid can most readily be prepared by heating ethyl anilidopyrotartaramate (50 grams) with potassium hydroxide (75 grams) and water (200 grams) in a reflux apparatus for 4 to 5 hours; the product is then boiled for half an hour without a condenser, acidified with hydrochloric acid, and converted into the copper salt which is then decomposed with hydrogen sulphide. It crystallises from water with 1 mol. H_2O , in lustrous, white prisms, melts at 111° in its water of crystallisation, and on further heating becomes solid, fusing again at 171° with decomposition. When it is heated at 180° for an hour in a closed tube, condensation ensues with the formation of pyranilpyroic anhydride, and a syrupy liquid from which the long, yellow needles of the former can readily be separated; these are then purified by crystallisation from dilute alcohol. Inasmuch as anilidopyrotartaric acid, $\text{COOH}\cdot\text{CMe}(\text{NPh})\cdot\text{CH}_2\cdot\text{COOH}$, yields the anhydride of pyranilpyroic acid, which on oxidation with permanganate, is converted into anilosuccinic acid, $\text{COOH}\cdot\text{C}(\text{NPh})\cdot\text{CH}_2\cdot\text{COOH}$, the

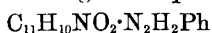
author considers that pyranilpyroic acid probably has the formula $\text{CO} \begin{smallmatrix} \text{NPh} \\ \diagup \\ \text{CH}_2 \end{smallmatrix} \text{CMe} \cdot \text{COOH}$, and that it assumes the labile form,



prior to the formation of its anhydride, which is regarded as a lactone

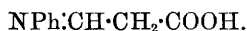


Pyranilpyrolactone (pyranilpyroic anhydride) can also be obtained by heating citraconic acid and aniline in molecular proportion at 170° until the decomposition is complete. It is identical with Gottlieb's citraconanil (*Annalen*, **77**, 277), melts at 98° and is slightly volatile with steam. It dissolves in alkalis forming alkaline salts of pyranilpyroic acid, and is soluble in hot mineral acids from which it crystallises unchanged on cooling. The *phenylhydrazide*,



(compare Wislicenus, *Abstr.*, 1887, 489), crystallises in small, lustrous, pure white needles, melts at $158\text{--}159^\circ$, and is readily soluble in alcohol and ether, but insoluble in water. The alkaline salts of pyranilpyroic acid decompose readily into aniline and citraconic acid when gently heated with mineral acids, and the acid decomposes in like manner when warmed with mineral acids or boiled with water. The *silver, lead, copper, tin, mercury, and iron* salts were prepared, and are sparingly soluble in water. On treatment with acetic chloride, acetic anhydride, phosphorus oxychloride, or phosphorus pentachloride, the acid is converted into pyranilpyrolactone; bromine does not react with it in the cold, and no definite product could be obtained from it by the action of sodium and ethyl iodide.

Anilsuccinic acid, $\text{COOH} \cdot \text{C}(\text{NPh}) \cdot \text{CH}_2 \cdot \text{COOH}$, is formed when pyranilpyroic acid (10 grams), dissolved in the calculated quantity of aqueous soda and mixed with 300 c.c. of water, is oxidised by potassium permanganate (18 grams) in 2 per cent. solution; after filtration, the product is treated with a solution of copper sulphate in the presence of sodium acetate, and the copper salt, after drying, is suspended in ether and decomposed by hydrogen sulphide. It crystallises in small, lustrous scales, melts at $151\text{--}152^\circ$, is readily soluble in alcohol and ether, soluble in benzene and water, sparingly soluble in light petroleum, and on boiling, its aqueous solution decomposes readily into acetic and oxanilic acids. The acid yields two series of salts, and of these *barium hydrogen anilosuccinate* crystallising in lustrous scales, and *sodium anilosuccinate* crystallising in small scales are the most characteristic; the normal salts can be dried at 100° without decomposition, but the hydrogen salts decompose when heated, yielding the corresponding salt of *β -anilpropionic acid*,



This acid can readily be obtained from its copper salt by treatment with hydrogen sulphide, and crystallises from water in small needles, containing $\frac{1}{2}$ mol. H_2O ; these melt at 153° and dissolve readily in alcohol,

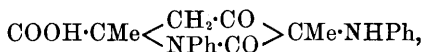
ether, benzene, and chloroform, but only sparingly in light petroleum. It is more stable than anilosuccinic acid, but decomposes in an analogous manner into formanilide and acetic acid when boiled with acids or alkalis. The *barium*, with 1 mol. H_2O , *copper*, with 1 mol. H_2O , *lead*, with 1 mol. H_2O , and *silver* salts are crystalline. When heated for some time at 170° , both anilosuccinic acid and β -anilopropionic acid yield γ -ketodihydroquinoline (this vol., p. 277) in small quantity together with carbanilide and oxanilide, and by way of explanation the author assumes that β -anilopropionic acid, prior to condensation, undergoes intramolecular change with the formation of β -anilidoacrylic acid.

γ -Ketodihydroquinoline, when heated with acetic anhydride, forms an *acetyl*-derivative, $\text{C}_9\text{H}_8\text{NO}\cdot\text{Ac}$ [$\text{Ac} = 1'$], which crystallises from alcohol or acetic acid in small needles, melts at 228° , and is readily soluble in boiling alcohol, acetic acid, and ether, sparingly soluble in benzene and chloroform, and insoluble in light petroleum and water. The *hydrazone*, $\text{C}_9\text{H}_7\text{N}\cdot\text{N}_2\text{HPh}$, crystallises from dilute alcohol in small, bright-yellow needles, melts at 168° , and is soluble in ether and alcohol. Since γ -ketodihydroquinoline does not undergo intramolecular change into the hydroxy-derivative [$\text{OH} = 4'$], the author is of opinion that ethyl anilacetate (Conrad and Limpach, Abstr., 1887, 679) would not yield γ -hydroxyquinoline if it had the constitution $\text{NPh}\cdot\text{CMe}\cdot\text{CH}\cdot\text{COOEt}$, and that consequently it must be regarded as ethyl β -anilbutyrate, $\text{CMe}(\text{NPh})\cdot\text{CH}_2\cdot\text{COOEt}$, which by condensation would yield the pseudo-form, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ \text{N}\cdot\text{CMe} \end{smallmatrix}\rangle$, and finally the hydroxy-derivative.

When dry pyranilpyroic acid, dissolved in hot acetic acid, is treated with zinc-dust, and the product after dilution with water and neutralisation is extracted with ether, *dihydropyranilpyroic acid*, $\text{CH}\cdot\text{OH}\langle\begin{smallmatrix} \text{NPh} \\ \text{CH}_2 \end{smallmatrix}\rangle\text{CMe}\cdot\text{COOH}$, is obtained. This crystallises in small, white needles, melts at 143° , and is soluble in alcohol and ether, sparingly soluble in benzene, chloroform, and water, and insoluble in light petroleum. It is far more stable than pyranilpyroic acid, and can be boiled with alkalis and mineral acids without decomposition. When heated above its melting point, or when treated with acetic chloride or acetic anhydride, it is converted into *dihydropyranilpyrolactone*, $\text{C}_{11}\text{H}_{11}\text{NO}_2$, which can also be obtained by distilling pyranilpyroic acid with zinc-dust in a current of carbonic anhydride. It forms small crystals, melts at 103° , dissolves readily in water, alcohol, ether, benzene, and chloroform, but only sparingly in light petroleum, and is converted into the acid without decomposition by boiling with alkalis. When treated with bromine-water, either in the cold or at 100° , dihydropyranilpyroic acid is converted into the *dibromide* of desoxy pyranilpyroic acid, $\text{C}_{11}\text{H}_{11}\text{NO}_2\text{Br}_2$, a colourless, crystalline compound, which yields *bromodesoxy pyranilpyroic acid*, $\text{CBr}\langle\begin{smallmatrix} \text{NPh} \\ \text{CH} \end{smallmatrix}\rangle\text{CMe}\cdot\text{COOH}$, when heated with aqueous soda. This melts at 165° , is readily soluble in alcohol and ether, sparingly soluble in water, and is destitute of basic properties; its *silver* salt crystallises

in small, lustrous forms which rapidly decompose. *Desoxypyranilpyroic acid*, $C_{11}H_{11}NO_2 + 1\frac{1}{2}H_2O$, is obtained from the bromo-derivative by treatment with sodium amalgam and water, and forms small crystals which melt at 136° , and are soluble in alcohol and water, readily soluble in ether, and sparingly in benzene and light petroleum.

The compound which is obtained along with pyranilpyrolactone by the decomposition of anilidopyrotartaric acid at 180° has the formula $C_{20}H_{18}N_2O_3$, and is separated from the former by treatment with ether until the residue, consisting of small scales, is white and free from the lactone. It crystallises from absolute alcohol in lustrous, white prisms, or by the slow evaporation of its ethereal solution in colourless, monoclinic prisms; $a : b : c = 0.5109 : 1 : 0.8069$; $\beta = 89^\circ 22'$; and is soluble in boiling alcohol and benzene, sparingly soluble in ether, and insoluble in water and light petroleum. When boiled with aqueous soda and the resulting solution neutralised with dilute sulphuric acid, it is converted into an acid, $C_{20}H_{19}N_2O_4$, which forms a white, microcrystalline powder, melts at 150° , and is readily soluble in excess of mineral acids, and in alcohol, ether, benzene, and acetone, sparingly soluble in water and chloroform, and insoluble in light petroleum and carbon bisulphide. The salts decompose readily, with the exception of the *sodium* salt, $C_{20}H_{19}N_2O_4Na$, which crystallises from water in silky scales. When dissolved in dilute sulphuric acid, and treated with a solution of potassium nitrite, it yields a compound, $C_{19}H_{17}N_3O_3$; this crystallises from absolute alcohol in lustrous, white needles, melts at 204° , and is readily soluble in benzene and chloroform, but sparingly soluble in alcohol, ether, and light petroleum. When the acid in boiling alcoholic solution is treated with sodium, it gives off an odour recalling that of the piperidine bases, and decomposes into aniline and a compound containing nitrogen. The author puts forward, under reserve, the view that these compounds are pyridine-derivatives, and ascribes to the acid the formula



regarding the compound $C_{20}H_{18}N_2O_3$ as its lactone, and the compound $C_{19}H_{17}N_3O_3$ as $CMe < \begin{smallmatrix} CH \cdot CO \\ NPh \cdot CO \end{smallmatrix} > CMe \cdot N(NO)Ph$. This view derives some support from the fact that glycollic acid is also formed in the condensation of anilidopyrotartaric acid, rendering it probable that a portion of the latter, by taking up the elements of a molecule of water, breaks up into the former and α -anilidopropionic acid, which then undergoes condensation with a molecule of anilidopyrotartaric acid forming phenyldiketodimethylanilidopiperidinecarboxylic acid and its lactone.

W. P. W.

Metallic Salts of Benzenesulphonic Acid. By T. H. NORTON and T. W. SCHMIDT (*Amer. Chem. J.*, 10, 136—140).—The following salts are described:— $(PhSO_3)_2Cd + 7H_2O$; $(PhSO_3)_2Mn + 6H_2O$; $(PhSO_3)_2Ni + 6H_2O$; $(PhSO_3)_2Co + 6H_2O$, and $PhSO_3Hg$; with the exception of the last, they are easily soluble in water. H. B.

Amine Salts of Benzenesulphonic Acid. By T. H. NORTON and J. H. WESTENHOFF (*Amer. Chem. J.*, **10**, 129—136).—No amine salts of the aromatic sulphonic acids have yet been described. The following derivatives of benzenesulphonic acid are all anhydrous, like the ammonium salts of the sulphonic acids, and unlike the metallic salts, which are generally hydrated; they are all readily soluble in alcohol and also in water, except the diphenylamine-derivative which is decomposed by water, and the orthotoluidine and α -naphthylamine salts which are only slightly soluble in cold water; they are generally insoluble in ether, benzene, or carbon bisulphide: those derived from the fatty amines are deliquescent: the dimethylaniline and methyl-diphenylamine salts could not be obtained in the crystalline condition. The methylamine salt melts at 147°; dimethylamine salt at 110°; trimethylamine salt at 88—89°; ethylamine salt, 92°; diethylamine salt, 139°; triethylamine salt, 120—121°; isobutylamine salt, 132°; isoamylamine salt, 107°; phenylamine salt, 235—237°; diphenylamine salt, 115—117°; orthotoluidine salt, 137°; and the α -naphthylamine salt melts at 225°. H. B.

Amine Salts of Paratoluenesulphonic Acid. By T. H. NORTON and A. H. OTTEN (*Amer. Chem. J.*, **10**, 140—145).—The free acid melts at 92°. Most of the amine salts are soluble in water; those of the aromatic amines crystallise easily, whilst the fatty amines yield salts which, on account of their greater solubility, are generally obtained only in radiocrystalline masses; the aromatic amine salts are more soluble in alcohol than the others, and have, moreover, a pronounced acid reaction, the others are neutral or alkaline. All are anhydrous. The methylamine salt melts at 125°; dimethylamine salt at 78°; trimethylamine salt at 92°; ethylamine salt at 111°; diethylamine salt at 88°; triethylamine salt at 65°; phenylamine salt at 223°; diphenylamine salt at 64°; orthotoluidine salt at 180°; and the α -naphthylamine salt melts at 239°. H. B.

Sulphimido-compounds. By P. T. CLEVE (*Ber.*, **21**, 1099—1100; compare Abstr., 1887, 834).—Further experiments have shown that by the action of hydriodic acid on the chlorides of nitrosulphonic acids, the SO_2Cl -group is attacked, the nitro-group remaining intact.

The reaction product of bromine and metanitrobenzenesulphonic chloride is a compound which yields metanitrobenzenesulphonamide when treated with ammonia, and metanitrobenzenesulphonic acid when acted on by dilute alcohol.

Diphenyl disulphide, $(\text{C}_6\text{H}_5)_2\text{S}_2$, melting at 61°, is formed by the action of hydriodic acid on benzenesulphonic chloride; similarly the chloride of β -naphthalenesulphonic acid yields β -dinaphthyl disulphide, melting at 139°. F. S. K.

2'-Phenylindole. By E. FISCHER and T. SCHMITT (*Ber.*, **21**, 1071—1077).—The product obtained by Möhlau from aniline and bromacetophenone, and the compound obtained by Fischer (Abstr., 1886, 805) from acetophenonephenylhydrazone are both identical with 2'-phenylindole (compare Möhlau, this vol., p. 483). They all melt

at 186°, give the same violet-blue, pine-wood reaction, the same nitroso-product and the same amidophenylindole melting at 174°.

Phenylacetaldehydephenylhydrazone, $\text{CH}_3\text{Ph}\cdot\text{CH}\cdot\text{N}_2\text{PhH}$, is obtained by mixing phenylhydrazine with phenylacetaldehyde, and warming the mixture; it crystallises from light petroleum in almost colourless forms, melting at 58°, and readily soluble in alcohol, ether, and benzene.

2'-Phenylindole is produced by heating the preceding compound with zinc chloride for 5 to 10 minutes at 180—185°; it crystallises from hot alcohol or benzene in thin leaves melting at 186°. This compound resembles methylketole in all its reactions, except in its behaviour towards nitrous acid.

Nitroso-2'-phenylindole, $[\text{Ph}:\text{NO} = 2':3']$ (Möhlau, Abstr., 1883, 342; Fischer, Abstr., 1886, 805), is best obtained by saturating a glacial acetic acid solution of the indole with a very concentrated solution of sodium nitrite. On heating quickly, it becomes darker coloured about 250°, and melts, not quite constantly, at about 258°, with decomposition. It is readily soluble in potash or soda, and is reprecipitated on addition of hydrochloric acid. It does not give Liebermann's reaction, but on reduction yields an amido-base, which has the closest resemblance to amidomethylketole (Wagner, this vol., p. 284).

Amido-2'-phenylindole, $[\text{NH}_2 = 3']$, is produced when the nitroso-compound is reduced with zinc and hydrochloric acid; it crystallises from hot benzene in thin, colourless, shining scales, which melt at 174°, and are almost insoluble in water, but dissolve readily in alcohol, ether, benzene, and dilute acids. It reduces Fehling's solution on boiling, and colours pine-wood orange. When in a moist condition, it is converted into a violet dye by oxidising agents, even by the oxygen of the air.

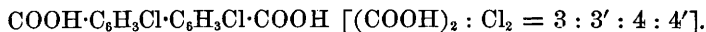
Benzylidene-2'-phenylindole, $\text{CHPh}(\text{C}_{14}\text{H}_{10}\text{N})_2$, is formed by heating the indole with benzaldehyde; it crystallises from hot acetone in slender, shining needles, which melt at 262—263°, and are very sparingly soluble in alcohol.

Hydro-2'-phenylindole, $\text{C}_{14}\text{H}_{13}\text{N}$, is obtained by boiling the indole with zinc and hydrochloric acid; it separates from light petroleum in almost colourless crystals, which melt at 46°, are readily soluble in dilute mineral acids, and colour pine-wood orange. Nitrous acid converts it into a nitrosamine. F. S. K.

Metaditolyl. By E. STOLLE (*Ber.*, **21**, 1096—1099).—*Metaditolyl*, $\text{MeC}_6\text{H}_4\cdot\text{C}_6\text{H}_4\text{Me}$, can be prepared by the action of nitrous acid and alcohol on orthotolidine, by heating orthodieresol with zinc-dust, or by the reduction of dichloroditolyl. It is a yellowish oil, boiling at 289°; its sp. gr. = 0.9993 at 16° (water at 4° = 1).

Dichloroditolyl, $\text{C}_6\text{H}_3\text{MeCl}\cdot\text{C}_6\text{H}_3\text{MeCl}$, is obtained from orthotolidine by Sandmeyer's method; the intermediate copper compound, $\text{C}_{12}\text{H}_6\text{Me}_2\text{N}_4\text{Cl}_2\cdot\text{CuCl}$, is a dark, yellowish-brown powder. Dichloroditolyl crystallises from alcohol in white, shining leaves, melting at 51°. On oxidation with chromic acid, it yields chlorotoluylic acid, melting at 205°. When heated with phosphorous pentachloride, a

compound, $C_{14}H_{10}Cl_4$, is formed, which on oxidation with dilute nitric acid yields *dichlorodiphenylmetacarboxylic acid*,



This acid is readily soluble in hot, sparingly in cold water, and melts at $267-268^\circ$.

Di-iododitolyl, $C_6H_3MeI \cdot C_6H_3MeI$, obtained by Sandmeyer's method, crystallises in yellow needles melting at $99-100^\circ$. F. S. K.

Aldines. By E. BRAUN and V. MEYER (*Ber.*, **21**, 1269—1282; compare this vol., p. 366).—Tetraphenylaldine* (Polonowska, this vol., p. 485) is prepared by gradually adding 5 per cent. sodium amalgam to a solution of benziloxime in aqueous soda. The product is filtered, washed with water, dried over sulphuric acid, and then rubbed with cold alcohol; it is again filtered, well washed with alcohol, dissolved in chloroform, and precipitated with alcohol. Finally it is dissolved in much boiling alcohol, from which it separates in slender, matted needles, melting at $245-246^\circ$. It is sparingly soluble, except in chloroform. Sulphuric acid dissolves it without change, yielding an intensely orange-coloured solution. It is not a base. The *tetranitro-derivative*, $C_{26}H_{16}N_8O_8$, melts at $130-140^\circ$, dissolves in chloroform and benzene, and is insoluble in ether, alcohol, and light petroleum.

An attempt was made to prepare diphenylaldine by reducing isonitroso-acetophenone with stannous chloride and hydrochloric acid. *Eso-amidoacetophenone hydrochloride*, $COPh \cdot CH_2 \cdot NH_2 \cdot HCl$, is formed. This salt separates from its aqueous solution in crystals melting at $183-184^\circ$. The *platinochloride* crystallises in long, slender, yellow needles melting at 200° . The *aurochloride* crystallises from water containing alcohol in slender, gold-coloured needles. The *sulphate* forms long crystals. The free base could not be isolated, as it decomposes when dried with formation of the compound $C_{16}H_{14}N_2O$. This crystallises from alcohol in stellate groups of slender needles, melting at $118-119^\circ$; it is readily soluble in hydrochloric acid. When *eso-amidoacetophenone hydrochloride* is treated with ammonia, instead of soda, iso-indole (diphenylaldine), $C_{16}H_{12}N_2$, is obtained (compare Wolff, *Ber.*, **20**, 432). The above compound was prepared by the action of alcoholic ammonia on bromacetophenone (Städel and Kleinschmidt, *Abstr.*, 659), and the two preparations compared.

Eso-amidoacetophenone is also formed by the action of ammonia on bromacetophenone.

When isonitrosomethyl ethyl ketone is reduced with stannous chloride and hydrochloric acid, a hydrochloride of a base is obtained not identical with tetramethylaldine; aldines of the fatty series are, therefore, not directly formed when isonitroso-ketones are reduced in acid solution.

N. H. M.

* Both the authors and Polonowska seem to have overlooked the fact that this substance is identical with the compound described as *ditolaneazotide* and as *tetraphenylazine* by Japp and Wilson (*Trans.*, 1886, 827), and by Japp and Burton (*Trans.*, 1886, 843, and 1887, 101).—ED.

Substitution in Benzoïn and in Analogues of Desoxybenzoïn and Benzyl Cyanide. By V. PÄPCKE (*Ber.*, **21**, 1331—1343).—Benzylated derivatives are obtained when the three tolyl cyanides are respectively treated with sodium ethoxide and benzyl chloride, hence the substitution of methyl in the phenyl-group in benzyl cyanide does not interfere with the displacement of one of the hydrogen-atoms of the methylene-group by an alkyl-radicle. Benzylated metatolyl cyanide, $C_6H_4Me \cdot CH(C_7H_7) \cdot CN$, is an oil which, after long standing, crystallises in rectangular tables, melts at 53° , and boils at $350\text{--}360^\circ$ with slight decomposition. On treatment with aqueous alkalis, it yields benzylated metatolylacetic acid, which separates from all solvents as an oil slowly solidifying to a crystalline mass which melts at $79\text{--}80^\circ$. Benzylated orthotolyl cyanide is an oil, and boils at $340\text{--}350^\circ$ with slight decomposition; the corresponding acid forms large crystals and melts at 95.5° . Benzylated paratolyl cyanide crystallises from alcohol in long, white needles, melts at 79° , and is insoluble in water, but soluble in alcohol; the corresponding acid crystallises from alcohol in small aggregates, melts at 105° , and is soluble in ether. It was not found possible to substitute a second benzyl-radicle for the remaining hydrogen-atom of the methylene-group in any one of these cyanides.

Benzoïn yields benzil only when acted on by sodium ethoxide, but forms a sodium-compound when its solution in benzene is treated with sodium; this derivative, however, contains more sodium than is required for the formula $CHPhBz \cdot ONa$. Acetylbenzoïn also, which melts at 83° and not at 75° (Zinin, *Annalen*, **104**, 120), does not react when treated with sodium ethoxide, but decomposes into its constituents, acetic acid and benzoïn. Lastly, *benzoïn isobutyl ether*, which can be prepared by heating benzoïn (10 grams), sodium (2 grams), alcohol (20 grams), and isobutyl bromide (20 grams) at 150° for four hours, and is an oil boiling at $240\text{--}245^\circ$ under 110 mm. pressure, does not form a benzylated derivative when treated with sodium ethoxide and benzyl chloride; from this it follows that it is not possible to effect a substitution of an alkyl-radicle for the hydrogen-atom of the methylene-group in benzoïn and its ethers.

Diphenyl benzyl ketone, $C_6H_5Ph \cdot CO \cdot CH_2Ph$, is prepared by dissolving phenylacetic chloride and diphenyl in molecular proportion in carbon bisulphide, treating the mixture with aluminium chloride in the cold, and finally heating at 100° in a reflux apparatus to complete the reaction. It crystallises from acetic acid and alcohol in lustrous scales, melts at 150° , and is insoluble in water, sparingly soluble in ether and cold alcohol. The *benzylated ketone*, $C_6H_5Ph \cdot CO \cdot CHPh \cdot C_7H_7$, is obtained by the action of sodium ethoxide and benzyl chloride; it crystallises in long, white needles, melts at 158° , is sparingly soluble in alcohol, and when heated for five hours at 160° with hydroxylamine hydrochloride is converted into the *oxime*, $C_{27}H_{22} \cdot N \cdot OH$, which crystallises in slender needles, and melts at 175° . On treatment with thiocarbonyl chloride, diphenyl benzyl ketone is converted into the compound $C_6H_5Ph \cdot CO \cdot CPh \cdot CS$ (compare this vol., p. 484); this has an intense yellow colour, melts at 320° , is insoluble in alcohol and ether, very sparingly soluble in chloroform, and dissolves in concen-

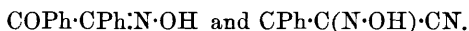
trated sulphuric acid with a green colour, which soon changes through violet to red, owing to the absorption of moisture.

Naphthyl benzyl ketone, $C_{10}H_7 \cdot CO \cdot CH_2Ph$, obtained in like manner from naphthalene, yields the corresponding alkyl-derivatives when treated with sodium ethoxide and ethyl bromide, isobutyl bromide, and benzyl chloride respectively. The products are oils, which cannot be crystallised, and do not yield crystalline oximes.

Fluoryl benzyl ketone, $C_{13}H_9 \cdot CO \cdot CH_2Ph$, obtained under like conditions from fluorene, crystallises in small, white tables, melts at 156° , and is sparingly soluble in alcohol and ether; the yield amounted to 5 per cent. only of the weight of fluorene employed. When treated with sodium ethoxide and benzyl chloride, it yields a *benzylated*-derivative, $C_{13}H_9 \cdot CO \cdot CHPh \cdot C_7H_7$, which crystallises from alcohol in slender, natted needles, melts at $149-150^\circ$, and is insoluble in ether, very sparingly soluble in hot alcohol. Fluoryl benzyl ketone reacts with thio-carbonyl chloride forming an orange-yellow powder, insoluble in alcohol and ether, but readily soluble in chloroform and benzene; although it could not be purified sufficiently for analysis, it probably has the composition $C_{13}H_9 \cdot CO \cdot CPh \cdot CS$, since it gives an intense colour reaction with concentrated sulphuric acid.

Acenaphthyl benzyl ketone, $C_{12}H_9 \cdot CO \cdot CH_2Ph$, formed in like manner from acenaphthene, crystallises in pale-yellow scales, melts at 114° , and is readily soluble in hot alcohol; the yield amounted to 30 per cent. of the weight of acenaphthene employed. On treatment with sodium ethoxide and benzyl chloride, it is converted into the *benzylated* derivative, $C_{12}H_9 \cdot CO \cdot CHPh \cdot C_7H_7$, which crystallises from alcohol in pale-yellow needles, and melts at 104° . In none of these ketones was it found possible to substitute an alkyl-radicle for the second hydrogen-atom of the methylene-group. W. P. W.

Negative Nature of Organic Radicles and the Question of the Existence of true Nitroso-compounds. By V. MEYER (*Ber.*, 21, 1291—1295).—The great analogy existing between ethyl malonate and acetoacetate on the one hand, and desoxybenzoïn and benzyl cyanide on the other was previously mentioned. The two latter compounds differ from the former in not yielding sodium compounds which can be isolated. Homologues of benzyl cyanide can be obtained by heating the cyanide with alkyl chlorides and solid potash. In like manner, derivatives of desoxybenzoïn can be prepared by using aqueous alcoholic potash. Desoxybenzoïn and benzyl cyanide are converted by nitrous acid into the isonitroso-derivatives,



Methyl-desoxybenzoïn, however, does not yield the nitroso-compound, $COPh \cdot CMePh \cdot NO$, but benzoic acid and acetophenoneoxime.

When diphenylacetoneitrile is treated with amyl nitrite and sodium ethoxide the polymeride described by Anschütz and Romig (*Abstr.*, 1886, 1033) is formed. It is probable that the nitroso-compounds (such as contain the group NO in direct combination with carbon) cannot exist; the pseudonitroses, the only class of compounds of which the nitroso-nature is generally undisputed, may be considered as nitrates

of the acetoximes, a view supported by Scholl's experiments (this vol., p. 443); thus, the formula of propylpseudonitrole would be $\text{CMe}_2\text{N}\cdot\text{O}\cdot\text{NO}_2$. (Compare this vol., p. 147.) N. H. M.

Negative Nature of Organic Radicles. Examination of Desoxybenzoïn. By V. MEYER and L. OELKERS (*Ber.*, 21, 1295—1306).—Desoxybenzoïn is prepared as follows:—20 grams of benzoïn, 60 grams of 75 per cent. alcohol, and 10 grams of granulated zinc are heated in a water-bath, treated with 20 grams of 80 per cent. alcohol saturated with hydrogen chloride, and the whole boiled for 2 to 3 hours. 10 grams of alcohol containing hydrochloric acid is then added, the liquid reduced to half its bulk by evaporation, and poured off from the unchanged zinc. The desoxybenzoïn is precipitated by hot water, the water poured off (on cooling more desoxybenzoïn separates) and the desoxybenzoïn made to solidify by cold water. It is pressed between filter-paper, distilled and then crystallised several times from alcohol. It melts at 60° and boils at $320\text{--}322^\circ$ (corr.). The yield of pure substance is 60 per cent. of the weight of the benzoïn used.

The introduction of alkyl-groups into desoxybenzoïn is carried out in the following manner:—A weighed amount of sodium is treated with absolute alcohol, the calculated amount of finely powdered desoxybenzoïn added, and the whole heated for two minutes on a water-bath. When cold, the alkyl-derivative is added and the mixture heated on a water-bath for 15 minutes.

Methyldesoxybenzoïn, $\text{COPh}\cdot\text{CHMePh}$, crystallises from alcohol, which dissolves it readily in long, slender needles, which melt at 53° , and boil at $317\cdot5\text{--}318\cdot5^\circ$ (corr.). The *oxime*, $\text{CHPhMe}\cdot\text{CPh}\cdot\text{N}\cdot\text{OH}$, crystallises in long, prismatic needles, melting at 120° . *Desoxybenzoïn oxime* crystallises similarly and melts at 98° .

Ethyldesoxybenzoïn, $\text{COPh}\cdot\text{CHEtPh}$, crystallises in long, slender needles, melts at 58° and boils at $323\text{--}324^\circ$ (corr.). The hydroxylamine-derivative crystallises from alcohol in needles melting at $129\text{--}130^\circ$.

Isobutyldesoxybenzoïn, $\text{C}_4\text{H}_9\cdot\text{CHPh}\cdot\text{COPh}$, prepared from isobutyl bromide, crystallises in short needles rather less soluble than the methyl and ethyl compounds; it melts at 78° and boils at $329\cdot5\text{--}330\cdot5^\circ$ (corr.). The hydroxylamine compound crystallises in prisms melting at 118° .

Benzyl-desoxybenzoïn, $\text{CH}_2\text{Ph}\cdot\text{CHPh}\cdot\text{COPh}$ (from benzyl chloride) crystallises in short, slender needles melting at 120° . It is very sparingly soluble in cold alcohol. The *oxime* crystallises from dilute alcohol in needles of a silvery lustre melting at 208° .

Attempts to introduce two alkyl-groups into desoxybenzoïn and to introduce a second alkyl-group into the derivatives described above gave negative results.

When a slow stream of nitrous acid is passed through sodium desoxybenzoïn, benzil monoxime is found. (Wittenberg and Meyer, *Abstr.*, 1883, 803.) The compound is most readily obtained by Claisen's method (*Abstr.*, 1887, 575), by adding 1 gram of desoxybenzoïn and 0·6 gram of amyl nitrite to a well-cooled solution of 0·12 gram of sodium in 3 to 4 grams of absolute alcohol; after two days the product is poured into water, shaken with ether, acidified

and then extracted with ether. The yield is 0.7 gram of pure isonitroso-compound.

Desoxybenzoïnacetic acid, $\text{COPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COOH}$, is prepared by adding 4 grams of ethyl chloracetate to 5 grams of desoxybenzoïn, 0.7 gram of sodium, and 7 grams of alcohol. It dissolves readily in aqueous potash, less in soda, and crystallises from alcohol in small tabular crystals melting at 156° . The silver salt was prepared. (Compare Knoevenagel, p. 706.) N. H. M.

Negative Nature of Organic Radicles. By R. RATTNER (*Ber.*, **21**, 1316—1322).—*Dibenzylacetoxime*, $\text{OH}\cdot\text{N}\cdot\text{C}(\text{C}_7\text{H}_7)_2$, forms yellowish crystals melting at 119.5° .

Dibenzyl dibenzyl ketone, $\text{CO}(\text{CHPh}\cdot\text{C}_7\text{H}_7)_2$, obtained by the action of benzyl chloride on dibenzyl ketone in presence of sodium, forms lustrous crystals melting at 121.5° . It is insoluble in water, readily soluble in ether, chloroform, and carbon bisulphide.

Methyl diphenylacetate, $\text{CHPh}_2\cdot\text{COOMe}$, crystallises from alcohol in plates melting at $59-60^\circ$. This salt and also methyl methylmandelate were treated with sodium ethoxide and isobutyl bromide, but with negative results.

Dibenzyl paraphenylene diacetonitrile, $\text{C}_6\text{H}_4[\text{CH}(\text{C}_7\text{H}_7)\text{CN}]_2$, is prepared in a manner similar to dibenzyl dibenzyl ketone. This when boiled with concentrated aqueous potash yields *potassium paraphenylenedibenzylidiacetate*. The *free acid* is obtained as a resin, and is purified by alternately boiling with calcium carbonate and precipitating with acid four or five times. It is a microcrystalline powder which melts at 251° and is insoluble in water, readily soluble in alcohol, ether, and chloroform. The *barium* and *silver* salts are described.

In the preparation of the nitrile an amorphous compound of the empirical formula $\text{C}_{14}\text{H}_{11}\text{N}_2$ is obtained. It is possibly formed by the condensation of 3 mols. of the cyanide with elimination of 2 mols. of hydrogen cyanide. It is insoluble in the usual solvents, soluble in hot phenol, and is very indifferent towards reagents.

Methyl phenylbenzoylacetate, $\text{COPh}\cdot\text{CHPh}\cdot\text{COOMe}$, is prepared by dissolving sodium in absolute alcohol, heating the product (after evaporating off the alcohol) at 200° in a stream of hydrogen; desoxybenzoïn dissolved in ether is added and heated at 200° until white fumes appear in the flask. The product is treated with ether and an excess of methyl chlorocarbonate, and heated on a water-bath. On adding water, an oil is obtained which is extracted with ether and dried over sulphuric acid. It cannot be otherwise purified, as when distilled it decomposes into stilbene, benzoic acid, and carbonic anhydride. If ethyl chlorocarbonate is used, stilbene is formed at once in large quantities. N. H. M.

Substitution in Organic Compounds containing Negative Radicles. By W. SCHNEIDEWIND (*Ber.*, **21**, 1323—1330).—V. Meyer has shown that one atom of hydrogen in the methylene-group present in benzyl cyanide and desoxybenzoïn can be displaced by an alkyl-group when either compound is treated with sodium ethoxide and an

alkyl iodide (this vol., p. 147). This reaction has been extended by the author to compounds containing in their formulæ two methylene- or methenyl-groups united together and each united with a negative radicle, and it is found that the nitrile of cinnamic acid, the nitrile of phenylpropionic acid, ethyl succinate, ethyl levulinate, benzalacetophenone, benzylacetophenone, and the nitrile of dibenzylacetic acid do not yield benzylated derivatives when respectively heated with the calculated quantities of sodium ethoxide and benzyl chloride at 103° until all alkaline reaction has disappeared.

Benzylacetophenone, $\text{COPh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$, could not be obtained by the action of aluminium chloride on a mixture of phenylpropionic chloride and benzene, but is formed by boiling benzalacetophenone in acetic acid solution with zinc-dust for 3 to 4 hours. It crystallises from alcohol in lustrous scales, melts at $72-73^{\circ}$, boils at above 360° without decomposition, and is insoluble in water, readily soluble in alcohol and ether. When oxidised with potassium permanganate, it yields carbonic anhydride and benzoic acid. The *oxime* crystallises in slender needles, melts at 87° , and is insoluble in water, readily soluble in alcohol and ether. The *phenylhydrazone* is an oil. The *isonitroso*-derivative, $\text{COPh}\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CH}_2\text{Ph}$, prepared by adding amyl nitrite (2 mols.) and then the ketone to sodium (2 at.) dissolved in 20 times its weight of alcohol, crystallises from ether in beautiful, pale-yellow forms, melts at $125-126^{\circ}$, and is readily soluble in alcohol and ether. Inasmuch as only one isonitroso-group could be introduced into the molecule of this compound, an attempt was made to prepare the di-isonitroso-derivative of the isomeric dibenzyl ketone but without success, since the product, which was formed in small quantity and crystallised in needles melting at $107-108^{\circ}$, contained too high a percentage of nitrogen.

The *nitrile* of dibenzylacetic acid, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CN})\cdot\text{CH}_2\text{Ph}$, is prepared by heating dibenzylacetamide and phosphorus pentachloride in molecular proportion dissolved in phosphorus oxychloride at 100° until evolution of hydrogen chloride ceases. It crystallises in white scales, or, by slow evaporation of its solutions, in tables, melts at $89-91^{\circ}$, and is insoluble in water, readily soluble in alcohol and ether. *Dibenzylacetamide* crystallises in white needles, melts at $128-129^{\circ}$, and is readily soluble in alcohol and ether, sparingly soluble in hot water.

Benzylcarbamine, $\text{CH}_2\text{Ph}\cdot\text{NC}$, is obtained by heating pure benzyl iodide dissolved in toluene with twice its weight of silver cyanide in a reflux apparatus for 3 to 4 hours. The product has the odour of the carbamines, boils chiefly at $220-221^{\circ}$, the thermometer afterwards gradually rising to 231° , and is a mixture of the carbamine with some benzyl cyanide. On treatment with sodium ethoxide and benzyl chloride, it yields benzylated phenylacetic acid (derived from the benzyl cyanide) and benzylamine only, hence the hydrogen of the methylene-group in benzylcarbamine unlike that in benzyl cyanide, is not displaceable by an alkyl-group under these conditions.

W. P. W.

Negative Nature of Organic Radicles. By E. KNOEVENAGEL (*Ber.*, 21, 1344—1354).—In the first portion of the paper, the author

gives the details of the experiments in which acetonitrile, isobutyronitrile, the nitrile of mandelic acid, diphenylmethane, triphenylmethane, fluorene, and the nitro-derivatives of these hydrocarbons were respectively treated with sodium ethoxide and benzyl chloride with negative results (compare this vol., p. 147).

Phenylbenzylsulphone, $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{Ph}$, is readily obtained by treating sodium benzenesulphinate dissolved in dilute alcohol with benzyl chloride. It is crystalline, melts at 148° , and is insoluble in water, sparingly soluble in ether and cold benzene, and dissolves in 60 parts of cold or 7 parts of boiling alcohol. It does not react with sodium ethoxide and benzyl chloride.

Desylacetic acid (desoxybenzoïnacetic acid, compare Meyer and Oelkers, p. 703), $\text{COPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COOH}$, is best prepared by adding desoxybenzoïn (1 mol.) to a solution of sodium (1 mol.) in 10 times its weight of alcohol, treating the product with acetic bromide (1 mol.) and heating it for 10 to 15 minutes on a water-bath. The product is then boiled for two hours in a reflux apparatus with 10 to 15 per cent. aqueous potash, diluted with water, shaken with ether to remove unaltered desoxybenzoïn, and the acid finally precipitated by addition of hydrochloric acid to the aqueous solution. The *copper, silver, zinc, lead, calcium, and barium* salts were prepared.

β -Desylpropionic acid, $\text{COPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$, is formed in like manner from desoxybenzoïn, sodium ethoxide, and ethyl β -iodopropionate. It crystallises from alcohol in slender, white, seemingly quadratic needles, melts at 136° , and is insoluble in water, readily soluble in ether and hot alcohol. The *silver, copper, zinc, barium and calcium* salts are described. The *methyl* salt, $\text{C}_{16}\text{H}_{15}\text{O}\cdot\text{COOMe}$, crystallises in colourless needles, melts at $63\text{--}64^\circ$, and is readily soluble in alcohol and ether, insoluble in water; the *ethyl* salt, $\text{C}_{16}\text{H}_{15}\text{O}\cdot\text{COOEt}$, crystallises in small, pale-yellow needles, melts at $33\text{--}34^\circ$, and is readily soluble in alcohol and ether. Hydroxylamine and phenylhydrazine react with the acid, yielding products which however could not be obtained in a state suitable for analysis.

α -Desylpropionic acid, $\text{COPh}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{COOH}$, is obtained under like conditions from desoxybenzoïn, sodium ethoxide, and α -bromopropionic acid. It crystallises from alcohol in slender, colourless needles, melts at $213\text{--}215^\circ$, and is less soluble in alcohol and ether than the β -acid. The *silver, copper, zinc, calcium and barium* salts were prepared.

W. P. W.

Bidesyls. By E. KNOEVENAGEL (*Ber.*, **21**, 1355—1361).—*Bidesyl*, $\text{COPh}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{COPh}$, is obtained, together with a small quantity of desylmalonic acid, by the action of sodium desoxybenzoïn (1 mol.) on ethyl bromomalonate (1 mol.) in alcoholic solution. It is also formed, together with isobidesyl, by heating desoxybenzoïn (1 mol.) with sodium (2 at. prop.) dissolved in 10 times its weight of alcohol, and adding to the cooled product an ethereal solution of iodine ($\frac{1}{2}$ mol.), and both compounds are formed when a mixture of desoxybenzoïn (1 mol.) and sodium ethoxide (1 mol.) in alcoholic solution is treated with desyl bromide (1 mol.). It crystallises from benzene in needles, melts at $254\text{--}255^\circ$, and is insoluble in water, ether, alcohol,

acids, and alkalis. When heated with hydroxylamine hydrochloride in alcoholic solution at 160° , it yields a compound which does not contain nitrogen; this crystallises from alcohol in lustrous forms, and melts at 171 – 172° .

Isobidesyl crystallises in colourless prisms, melts at 160 – 161° , and is readily soluble in hot alcohol and benzene, sparingly soluble in ether and light petroleum. Like *bidesyl*, it is optically inactive, and both compounds when heated under like conditions boil almost simultaneously at about 340° . When boiled with hydroxylamine hydrochloride (3 to 4 mols.) and aqueous potash (2 mols.) on a water-bath in a reflux apparatus for four hours, *isobidesyl* is converted into a compound, $C_{56}H_{47}N_3O_4$, which melts between 110 – 120° , and is extremely soluble in cold alcohol, ether, and benzene, but insoluble in light petroleum. The research is being continued.

Desyl bromide, $CHPhBr \cdot CPh$, can be obtained in almost quantitative yield by treating desoxybenzoïn with bromine by Staedel and Kleinschmidt's method for the preparation of bromacetophenone from acetophenone (Abstr., 1880, 659). It melts at 54 – 55° .

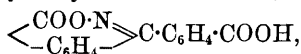
Ethyl bromomalonate, $COOEt \cdot CHBr \cdot COOEt$, is prepared by adding bromine (1 mol.) to ethyl malonate (1 mol.), distilling, and collecting the fraction boiling at 230 – 236° .
W. P. W.

Diphthalic Acid. By P. JULLARD (*Chem. Centr.*, 1887, 1143–1145; *Arch. sci. phys. nat.* [3], 17, 502–535, and 18, 24–62).—Diphthalic acid, $C_2O_2(C_6H_4 \cdot COOH)_2$, is formed in good quantity by oxidising diphthallyl with potassic permanganate, or with potassic hypobromite or hypochlorite; it melts at 272° . The *ethyl* salt melts at 154° . If the acid is heated at about 110° with 40 per cent. caustic alkali, *hydroxydiphenylmethanetricarboxylic acid*,

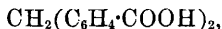


is formed, which, however, exists only in combination with bases; when liberated by the action of an acid, it is converted into the lactone. By heating the solution, *phthalidecarboxylic acid* is formed. With strong bases it deports itself as a tribasic acid, with ammonia and barium hydrate as a bibasic acid. The ethyl salt melts at 108° . Phosphorus and hydriodic acid reduce it to *diphenylmethanetricarboxylic acid*, $CH(C_6H_4 \cdot COOH)_2 \cdot COOH$, which crystallises with 1 mol. H_2O . At about 200° it melts, and at 250° is transformed into a beautiful, red substance melting at 260° . If diphthalic acid is heated with 50 to 55 per cent. potash at 125 – 130° , *hydroxydiphenylmethanedicarboxylic acid*, $OH \cdot CH(C_6H_4 \cdot COOH)_2$, is formed, which is transformed into the lactone on being liberated. The latter, $CO \langle \begin{smallmatrix} C_6H_4 \\ O \end{smallmatrix} \rangle CH \cdot C_6H_4 \cdot COOH$, melts at 205° . With potash and soda it acts as a bibasic acid, with ammonia as a monobasic acid only. The methyl salt melts at 154 – 155° , the ethyl salt at 99.5° . Alcoholic ammonia reacts with the ethereal salt with formation of an amide, $C_{14}H_{10}O_2 \cdot CONH_2$, melting at 158 – 160° . With nitrosulphuric acid, a dinitro-acid is formed, melting at 270 – 280° . By oxidation with alkaline potassic permanganate, benzophenonedicarboxylic acid is formed, whilst chromic

acid in glacial acetic acid oxidises phenylphthalidecarboxylic acid to a dilactone, $\langle \text{C}_6\text{H}_4 \rangle \text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{COO} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{O} \cdot \text{CO} \end{smallmatrix} \rangle$, which is also formed by heating benzophenonedicarboxylic acid either in the dry state or in solution. The salts of barium, copper, and silver, as well as the methyl and ethyl salts were prepared. It reacts with phenylhydrazine without loss of water. The hydroxylamine-derivative,



melts at 213—215°. The dilactone is extremely stable, and is only transformed into the acid when boiled with alkali. With fuming sulphuric acid it forms a sulphonic acid, which on fusion with potash gives alizarin. Aqueous and also alcoholic ammonia react with the dilactone, the former with production of an imide melting at 251—252°, the latter with production of a diimide which melts at 284—285°. Phenylphthalide mono- and di-carboxylic acids, and also the dilactone, are reduced by hydriodic acid and phosphorus at 170—180° with formation of *diphenylmethanedicarboxylic acid*,



melting at 254—255°. If the temperature of the reaction with the dilactone is allowed to rise to 210—220°, anthranolcarboxylic acid is formed; this melts at 252—253°. J. W. L.

Derivatives of Orthotolidine. By P. L. HOBBS (*Ber.*, **21**, 1065—1068).—*Diacetylorthotolidine*, $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2$, crystallises from hot acetic acid in slightly-coloured needles which melt above 310°, and are only sparingly soluble in ordinary solvents. *Dibenzoylorthotolidine*, $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_2$, crystallises from hot acetic acid in snow-white needles melting at 259°; it is insoluble in ordinary solvents. The condensation-product of orthotolidine and phthalic anhydride, $\text{C}_{30}\text{H}_{20}\text{N}_2\text{O}_4$, crystallises from benzene in dark-brown needles melting at 307°. The *urethane*, $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4$, crystallises from alcohol in large, pale-red needles melting at 187°. The *formyl*-derivative, $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$, forms microscopic needles which melt at 254°; on distillation, a compound is obtained which melts at 121°, and has the properties of an amidine. *Tolyldithiocarbimide*, $\text{C}_{16}\text{H}_{12}\text{N}_2\text{S}_2$, crystallises from benzene in large, transparent plates melting at 157°.

Orthodicrosol, $\text{C}_{14}\text{H}_{14}\text{O}_2$, crystallises from water in slightly-coloured, large, broad needles melting at 157°.

Benzoylorthodicrosol, $\text{C}_{28}\text{H}_{24}\text{O}_4$, crystallises from glacial acetic acid in long needles melting at 185°. The *acetyl*-derivative, $\text{C}_{18}\text{H}_{18}\text{O}_4$, forms long needles melting at 131°. The *ethyl*-derivative melts at 156°. The *propyl*-derivative crystallises from alcohol in snow-white leaves. The *amyl*-derivative crystallises from amyl alcohol in thick needles or prisms, which are readily soluble in alcohol and ether, and melt at 69°. (Compare Gerber, this vol., p. 484.) F. S. K.

Action of Chlorine on Phenols. By T. ZINCKE (*Ber.*, **21**, 1027—1048).—*Ketochloride* is the generic name given to the ketone-like products obtained by the action of chlorine on phenols.

Dichlor- α naphthol, $C_{10}H_5Cl_2 \cdot OH$ [$OH : Cl_2 = 1 : 2 : 4$], is the first product which can be isolated of the action of chlorine on α -naphthol in glacial acetic acid solution; it is also formed by the reduction of tri- and penta-chloroketonaphthalene (see below). It crystallises from glacial acetic acid in thick, transparent needles, which lose acetic acid, become dull, and disintegrate on exposure to the air; it crystallises from benzene and alcohol in slender, shining needles, which melt at $107-108^\circ$, dissolve readily in ether, benzene, and absolute alcohol, and also in sodium carbonate with evolution of carbonic anhydride. It is readily oxidised by chlorine or bromine with formation of an insoluble, blue substance, which, on further treatment with the halogen, becomes yellow. This blue compound is also formed by the action of trichloroketonaphthalene. By careful oxidation with nitric acid, dichlor- α -naphthol yields chlor- α -naphthaquinone. The *acetyl*-derivative, $C_{10}H_5Cl_2 \cdot OAc$, is readily soluble in glacial acetic acid and alcohol, and crystallises from the latter in thick, colourless needles, melting at $74-76^\circ$.

Trichlor- α -naphthol, [$Cl_3 = 2 : 3 : 4$], is obtained by reducing pentachloroketonaphthalene with alkaline sulphites; it crystallises from glacial acetic acid or benzene in long, colourless, silky needles, melts at $159-160^\circ$, is readily soluble in ether, less readily in warm, sparingly in cold alcohol or glacial acetic acid. The *acetyl*-derivative forms long, white, shining needles, which are moderately soluble, and melt at $123-124^\circ$. Trichlor- α -naphthol yields dichloro- β -naphthaquinone, and a small quantity of dichlor- α -naphthaquinone, when carefully oxidised with nitric acid in acetic acid solution, but with chromic acid the chief product is dichlor- α -naphthaquinone.

Trichlor- α -ketonaphthalene, $C_6H_4 \begin{smallmatrix} CO \cdot CCl_2 \\ CCl \cdot CH \end{smallmatrix}$ or $C_6H_4 \begin{smallmatrix} CO \cdot CCl \\ CCl_2 \cdot CH \end{smallmatrix} \gg$ (chlor- α -naphthaquinone chloride), is the second product of the action of chlorine on α -naphthol in glacial acetic acid solution; it crystallises in large, characteristic, transparent, flat, monoclinic prisms, melting at $120-121^\circ$, is very readily soluble in benzene, less so in glacial acetic acid, and sparingly in alcohol. This compound can also be obtained by the action of chlorine on dichlor- α -naphthol. When boiled with dilute alcohol or dilute acetic acid, it yields chlor- α -naphthaquinone, $C_6H_4 \begin{smallmatrix} CO \cdot CCl \\ CO \cdot CH \end{smallmatrix} \gg$. This crystallises from alcohol and dilute acetic acid in shining, yellow needles, which melt at $117-118^\circ$, and are readily soluble in benzene, sparingly in ether. When treated with chlorine in glacial acetic acid solution, it is converted into dichlor- α -naphthaquinone, and alkalis transform it slowly, with partial decomposition, into chlorohydroxynaphthaquinone. Treated with aniline, it yields chloranilido- α -naphthaquinone, which can also be obtained from dichloronaphthaquinone.

Trichloroketonaphthalene can be readily reduced to dichlor- α -naphthol, and when treated with aniline it yields anilidonaphthaquinonanilide. By the action of hydroxylamine hydrochloride on trichloroketonaphthalene, three different nitrogenous products are formed, two of which are insoluble in sodium carbonate; one of these

is probably a true nitroso-compound, $C_{10}H_5Cl_2NO$ [$NO : Cl_2 = 1 : 2 : 4$]. The product which is soluble in sodium carbonate appears to be a *monoxime*; it melts at $146-149^\circ$, and decomposes at 170° . The third product is sparingly soluble, and melts at 205° .

Tetrachlor- α -ketonaphthalene, $C_6H_4<\begin{smallmatrix} CO \cdot CCl_2 \\ CCl_2 \cdot CCl \end{smallmatrix}>$ (or dichlor- α -naphthaquinone chloride, $C_6H_4<\begin{smallmatrix} -CO \cdot CCl \\ CCl_2 \cdot CCl \end{smallmatrix}>$), was obtained in two different modifications, which perhaps have different constitutions as expressed by the above formulæ. Both compounds are formed by treating trichlor- α -naphthol with chlorine. The α -modification crystallises from glacial acetic acid in small, transparent rhombohedra, which, when taken from the solution, become yellow, and keep their colour when recrystallised from ether; it is rather easily soluble in hot alcohol or hot glacial acetic acid, and melts at $104-105^\circ$.

The β -modification crystallises from ether in shining, colourless, transparent, rhombic forms, which are combinations of prisms and pyramids; it melts at $93-94^\circ$, and becomes amethyst-coloured on exposure to light.

The β -modification can also be obtained by treating an alcoholic solution of the pentachloride (see below) with dilute alkali, or by boiling an alcoholic solution of the α -modification; in the latter case, dichlor- α -naphthaquinone is also formed.

These two modifications of tetrachlor- α -ketonaphthalene are very similar in their general behaviour; they are both converted into dichlor- α -naphthaquinone when boiled with dilute alcohol or dilute acetic acid; when warmed with dilute alcoholic potash, they yield chlorhydroxynaphthaquinone, and when treated with concentrated potash and a few drops of alcohol, they are converted into dichlor-indenehydroxycarboxylic acid, which can be recognised by transforming it into dichloroketoindene, $C_6H_4<\begin{smallmatrix} CO \\ CCl \end{smallmatrix}>CCl$.

When potash is gradually added to a solution of the tetrachloride in absolute alcohol, long, orange-red shining needles, melting at $148-149^\circ$, are obtained. This compound, which can also be obtained from the pentachloride, appears to be the ethyl-derivative of chlorhydroxynaphthaquinone, $C_6H_4<\begin{smallmatrix} CO \text{ --- } CO \\ C(OEt) : CCl \end{smallmatrix}>$; it yields β - β -chlorhydroxy- β -naphthaquinone anilide when treated with aniline, and is converted into chlorhydroxynaphthaquinone by the action of alkalis.

The corresponding *propyl*-derivative is obtained by treating a propyl-alcoholic solution of the tetrachloride with potash in a similar manner; it is a yellowish-red, crystalline compound, which melts at 190° , and gives β - β -chlorhydroxynaphthaquinoneanilide when treated with aniline.

Tetrachloroketonaphthalene is converted into trichlor- α -naphthol by reducing agents; when treated with potassium iodide, iodine is liberated, amorphous insoluble compounds are obtained, and dichlorhydroxynaphthaquinone appears to be formed. It yields a mixture of various nitrogenous compounds when treated with hydroxylamine

hydrochloride, and combines with aniline to form chloranilidonaphthaquinoneanilide (see below).

Pentachloroketohydronaphthalene, $C_6H_4<\begin{smallmatrix} CO-CCl_2 \\ CCl_2\cdot CHCl \end{smallmatrix}>$, is obtained by saturating a glacial acetic acid solution of α -naphthol with chlorine in the cold. It is readily soluble in hot benzene, from which it crystallises in colourless, almost right-angled, monoclinic plates, melting at $156-157^\circ$; it is very sparingly soluble in ether, sparingly in alcohol, but more readily in hot glacial acetic acid, from which it crystallises in hard, thick forms. When heated above its melting point, it becomes slightly coloured, and at about $200-220^\circ$ evolution of hydrogen chloride commences. It is readily converted into tetrachloroketonaphthalene, and yields, therefore, with various reagents the same products as the two tetrachloroketones. Stannous chloride transforms it into trichloroketone, which on further reduction gives α - β -dichlor- α -naphthol. Alkaline sulphites, in acetic acid solution, and phenylhydrazine, convert it into trichlor- α -naphthol; potassium iodide acts similarly, tetrachloroketone being first formed. By continued boiling with alcohol, it yields small quantities of tetrachloroketonaphthalene, part of which is further transformed into dichlor- α -naphthaquinone. This last-named compound is obtained almost quantitatively on heating the pentachloride in sealed tubes at $120-130^\circ$ with dilute alcohol or dilute acetic acid. When the pentachloride is treated with alkalis, the products, which vary according to the conditions of the experiment, are the same as those produced from tetrachloroketonaphthalene.

β - β -Chloranilidonaphthaquinone anilide, $C_6H_4<\begin{smallmatrix} CO\cdot C(NHPh) \\ -C(NPh)\cdot CCl \end{smallmatrix}>$, is formed when aniline is added to an alcoholic solution of the pentachloroketone; it crystallises from benzene in dark-red, shining needles, which melt at 157° , and are only sparingly soluble in alcohol and glacial acetic acid. The salts of this base are bluish-black, and are readily decomposed by alcohol or water. The *platinochloride*, $(C_{22}H_{15}ClN_2O)_2\cdot H_2PtCl_6$, crystallises in small black-violet leaves with a metallic lustre. The anilide yields chloranilidonaphthaquinone when boiled with alcoholic hydrochloric acid.

Hexachloroketohydronaphthalene, $C_6H_4<\begin{smallmatrix} -CO\cdot CCl_2 \\ CCl_2\cdot CCl_2 \end{smallmatrix}>$, is obtained by heating the tetrachloride with manganese dioxide and hydrochloric acid; when crystallised slowly from glacial acetic acid, it forms thick, hard, seemingly monoclinic forms, but when crystallisation proceeds slowly, long striated needles are obtained. It is readily soluble in benzene and hot alcohol, sparingly soluble in ether, and melts at 130° ; when heated above this temperature, it loses chlorine. This compound is tolerably stable, it liberates iodine from potassium iodide only slowly, and does not react with aniline; it is converted into trichlor- α -naphthol by the action of reducing agents. When treated with alkalis in alcoholic solution, the ring is split, and an acid, $COOH\cdot C_6H_4\cdot CO\cdot CCl_2\cdot CCl_2$, is obtained, which is identical with that produced from tetrachlorodiketonaphthalene (this vol., p. 490). This acid crystallises from dilute alcohol, or dilute acetic acid, in colour-

less, acute-angled rhombohedra, or in leaves which melt at 127—128°. When heated with concentrated sulphuric acid, it loses hydrochloric acid, and is converted into a compound which is probably a substituted hydrindenecarboxylic acid. F. S. K.

β -Tetrahydronaphthylamine. By E. BAMBERGER and R. MÜLLER (*Ber.*, **21**, 1112—1125; compare this vol., pp. 159, 599).—In its behaviour towards diazobenzene chloride, β -tetrahydronaphthylamine resembles the non-aromatic amines, and yields a *diazoamido*-derivative, $C_{10}H_{11}\cdot NH\cdot N_2Ph$, which combines with picric acid in ethereal solution to form a *picrate* crystallising in lustrous, ruby-red needles and melting at 118°. Diazoamidotetrahydro- β -naphthylamine is explosive, is volatile with steam, and when heated with dilute acids is decomposed for the most part into nitrogen, aniline, and dihydronaphthalene, a small quantity of β -tetrahydronaphthylamine and, probably, phenol being also formed. The tetrahydro-base is not attacked when boiled even for a day with hydrobromic acid (containing 47.8 per cent. of hydrogen bromide), but when heated with the acid at 150—160° is slowly decomposed into naphthalene, ammonia, and hydrogen; a similar result is also obtained by heating the base in sealed tubes at 80—100° above its boiling point for several days. The nitrite does not decompose below 160°, but when heated at 180—190° is converted into nitrogen, water, and dihydronaphthalene, together with some ammonia formed by a secondary reaction. The aqueous solution of a mixture of the tetrahydro-base and nitrous acid in molecular proportion is not affected by prolonged boiling, and only suffers decomposition to a slight extent when heated at 120—130° for 20 hours, naphthalene being formed; the solution of a similar mixture in dilute sulphuric acid (1 : 10) is, however, less stable, and decomposes on warming with the production of naphthalene and a small quantity of an oil. The formation of naphthalene, taken in conjunction with the fact that a certain proportion of the tetrahydro-base remains unchanged in these decompositions, renders it probable that the reaction proceeds normally with the formation of nitrogen, water, and a hydronaphthol, which then decomposes into water and dihydronaphthalene, the latter being finally oxidised to naphthalene at the expense of a portion of the nitrous acid. To avoid if possible this secondary reaction, amyl nitrite was employed as the diazotising agent instead of nitrous acid, with the result that dihydronaphthalene, amyl alcohol, nitrogen, and water were obtained.

Acetyltetrahydro- β -naphthylamine does not react with bromine in chloroform solution at 0°, from which the authors conclude that one of the two benzene nuclei is completely hydrogenated. To determine which, the tetrahydro-base was oxidised by suspending 3 grams in 250 c.c. of water containing a small quantity of sodium carbonate in solution, cooling to 10—12°, and adding in small quantities at a time 9 to 10 grams of a 4 per cent. permanganate solution; much ammonia escaped, and phthalic acid, together with Gabriel and Michael's hydrocinnamorthocarboxylic acid, $COOH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot COOH$ (*Abstr.*, 1878, 426; this vol., p. 150), which constitutes the chief product

under these conditions, were obtained, hence β -tetrahydronaphthylamine has the constitution $[H_2 : H_2 : H, NH_2 : H_2 = 1 : 2 : 3 : 4]$.

Valeryl- β -naphthylamine, $C_{10}H_7 \cdot NH \cdot CO \cdot C_4H_9$, is formed in small quantity by the action of sodium on a boiling solution of β -naphthylamine in valeric acid; it crystallises in long, vitreous prisms, and melts at 138.5° .

W. P. W.

Derivatives of Diamido- α -naphthol. By S. MEERSON (*Ber.*, **21**, 1195—1199).—*Diamido- α -naphthol hydrochloride*, $OH \cdot C_{10}H_5(NH_2, HCl)_2$, can be prepared from the stannochloride obtained when Martius' yellow is reduced with tin and hydrochloric acid, by suspending it in water, precipitating the tin with hydrogen sulphide, evaporating the filtrate in a vacuum, and treating the residue with concentrated hydrochloric acid. It crystallises in colourless, microscopic tables, and is fairly stable in the dry state. When treated with anhydrous sodium acetate and acetic anhydride, it is converted into *triacetyldiamido- α -naphthol*, $C_{10}H_5(OAc)(NHAc)_2$, which crystallises from acetic acid in white, microscopic needles, melts at 280° with decomposition, and is insoluble in water, sparingly soluble in boiling alcohol. It dissolves also in dilute aqueous potash with a red colour, and is oxidised to *acetamidonaphthaquinone*, $C_{10}H_5O_2 \cdot NHAc$, when the solution is acidified with hydrochloric acid and treated with ferric chloride. The quinone crystallises from alcohol in lustrous, golden-yellow scales, and melts at 198° with decomposition.

Nitrotriacetyldiamido- α -naphthol, $NO_2 \cdot C_{10}H_4(OAc) \cdot (NHAc)_2$, is obtained when triacetyldiamido- α -naphthol suspended in acetic acid is treated in the cold with nitric acid (sp. gr. = 1.48) until solution occurs. It is a yellow, granular powder, melts at 235° with decomposition, and on oxidation with potassium permanganate yields phthalic acid. Fuming hydrochloric acid dissolves it on warming with the formation of *nitrodiamidoethenyl- α -naphthol hydrochloride*,

$CMe \leq \overset{O}{N} > C_{10}H_4(NO_2) \cdot NH_2, HCl$ [$O : N : NO_2 : NH_2 = 1 : 2 : 3 : 4$],

which crystallises in long, slender, lustrous, citron-yellow needles, and yields a *platinochloride*, $(C_{12}H_9N_3O_3)_2, H_2PtCl_6$, crystallising in dark-yellow needles. On treatment with water, the hydrochloride decomposes, yielding the *base*, which has a beautiful scarlet colour, and is only sparingly soluble in alcohol; by boiling with very dilute aqueous potash, it is converted into *hydroxynitroethenylamido- α -naphthol*,

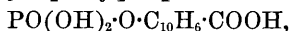
$CMe \leq \overset{O}{N} > C_{10}H_4(NO_2) \cdot OH$; this crystallises in slender, brown needles,

and melts at 163° with decomposition.

Acetamidonaphthaquinoneacetimide, $NAC \cdot C_{10}H_5O \cdot NHAc$, is prepared by the action of anhydrous sodium acetate and acetic anhydride on diimido- α -naphthol hydrochloride. It crystallises from alcohol in thick, dark-yellow prisms, and melts at 178° with decomposition. On oxidation with nitric acid (sp. gr. = 1.48), it yields the acetamidonaphthaquinone already described, and on treatment with bromine (1 mol.) in acetic acid solution is converted into *bromacetamidonaphthaquinone*, $C_{10}H_4O_2Br \cdot NHAc$, which crystallises from alcohol in lustrous, golden-yellow needles, and melts at 205° with decomposition.

W. P. W.

Action of Phosphorus Pentachloride on α -Hydroxynaphthoic Acid. By R. WOLFFENSTEIN (*Ber.*, **21**, 1186—1192; compare Abstr., 1887, 963).— α -Carboxynaphthylphosphoric acid,



is prepared either by heating α -chlorocarboxynaphthylorthophosphoric dichloride at 90° for several days until the weight is constant, or by allowing it to remain in contact with water for three weeks. It crystallises in slender, white needles, is readily soluble in acetone, less soluble in benzene, and though stable when dry, decomposes readily in aqueous solution into α -hydroxynaphthoic acid and phosphoric acid. The *silver* salt, $\text{C}_{11}\text{H}_6\text{PO}_6\text{Ag}_3$, and *lead* salt, $(\text{C}_{11}\text{H}_6\text{PO}_6)_2\text{Pb}_3$, were prepared; the ammonium salt decomposes in aqueous solution into ammonium α -hydroxynaphthoate. The action of hot acetic acid on the dichloride resembles that of water, since α -carboxynaphthylphosphoric acid is first formed, and this on further heating with the acid is converted into α -hydroxynaphthoic acid and phosphoric acid.

α -Chlorocarboxynaphthylorthophosphoric dichloride when treated with absolute alcohol (5 mols.) in the cold, yields a *diethyl* salt, $\text{PO}(\text{OEt})_2 \cdot \text{O} \cdot \text{C}_{10}\text{H}_7 \cdot \text{CCl}_3$, which is crystalline, melts at 63° , and decomposes when boiled with water. Phosphorus pentachloride reacts with the dichloride under pressure at 180° , forming α -chloronaphthoic tri-chloride, $\text{C}_{10}\text{H}_6\text{Cl} \cdot \text{CCl}_3$. This crystallises in colourless rhombohedra, melts at 73° , dissolves readily in the ordinary solvents, and gives the malachite-green reaction on boiling with dimethylaniline and zinc chloride. When boiled with water and acetic acid, it is converted into a *chloronaphthoic acid*, $\text{C}_{10}\text{H}_6\text{Cl} \cdot \text{COOH}$ [probably $\text{Cl} : \text{COOH} = 1 : 2$], which crystallises from benzene in slender, white needles, melts at 196° , and yields β -naphthoic acid on treatment with sodium amalgam. The *silver* salt, $\text{C}_{10}\text{H}_6\text{Cl} \cdot \text{COOAg}$, and *calcium* salt, $(\text{C}_{10}\text{H}_6\text{Cl} \cdot \text{CO}_2)_2\text{Ca} + 2\text{H}_2\text{O}$, of this acid were prepared.

W. P. W.

Anthranol. By F. GOLDMANN (*Ber.*, **21**, 1176—1182).—Anthraquinone dichloride is obtained when a chloroform solution of anthranol is treated with dry chlorine. It crystallises in thin, pale-yellow monoclinic prisms, $a : b : c = 0.7973 : 1 : 0.6262$; $\beta = 72^\circ 48'$; faces observed, ∞P , 0P , and $-\text{P}$; it melts at 132 — 134° , and is identical with Thörner and Zincke's compound (Abstr., 1878, 231). Anthraquinone dibromide (Abstr., 1887, 1049) crystallises in pale-yellow, monoclinic forms, $a : b : c = 1.5009 : 1 : 1.4708$; $\beta = 70^\circ 43'$; faces observed, 0P , $-\text{P}$, $+\text{P}$, $\frac{1}{2}\text{P}\infty$, and $+2\text{P}2$.

When finely powdered anthranol (15 grams) dissolved as far as possible in boiling aqueous potash (15 grams) is heated with an excess of ethyl iodide (40 grams) in a reflux apparatus for 10 to 12 hours, an oil is obtained consisting of anthranyl ethyl ether and diethylanthrone; these can readily be separated, as the former is dissolved whilst the latter is precipitated in a crystalline form when the product is treated with light petroleum.

Anthranyl ethyl ether, $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{OEt}) \\ | \\ \text{CH} \end{array} \text{---} \text{C}_6\text{H}_4$, is a heavy, yellow oil,

and dissolves readily in benzene, light petroleum, ether, alcohol, and acetic acid, yielding solutions showing a blue fluorescence. It could not be crystallised. On oxidation with chromic acid in acetic acid, it yields anthraquinone, and when dissolved in carbon bisulphide cooled at 15—20° and treated with bromine, it is converted into a yellow or red crystalline product which decomposes at the ordinary temperature into hydrogen bromide and *dibromanthranyl ethyl ether*,

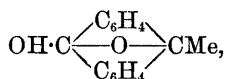


This forms small, colourless crystals, melts at 116—117°, decomposes with the evolution of bromine and hydrogen bromide on further heating, and is soluble in benzene. On oxidation with chromic acid in acetic acid solution, it yields a derivative, $\text{C}_{16}\text{H}_{13}\text{O}_3\text{Br}$, which crystallises from benzene and light petroleum in large needles, and melts at 135—138°; further oxidation converts it seemingly into bromanthraquinone.

Diethylanthrone, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CEt}_2 \\ \text{CO-} \end{smallmatrix} > \text{C}_6\text{H}_4$, crystallises in colourless forms, melts at 136°, and is readily soluble in benzene, chloroform, alcohol, and ether, soluble in light petroleum, and insoluble in aqueous alkalis. It is slowly oxidised to anthraquinone by chromic acid in acetic acid solution, does not react with bromine in carbon bisulphide solution, and is not affected by heating at 180° with a solution of hydrogen chloride in acetic acid. When heated with hydriodic acid (sp. gr. = 1.7) and amorphous phosphorus at 180—200° for three hours, it is reduced to *diethylhydroanthracene*, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CEt}_2 \\ \text{CH}_2 \end{smallmatrix} > \text{C}_6\text{H}_4$, which crystallises in colourless forms, melts at 48—50°, dissolves readily in light petroleum, benzene, ether, and carbon bisulphide, and is oxidised to diethylanthrone by chromic acid in acetic acid solution.

W. P. W.

Methyloxyanthranol. By C. LIEBERMANN (*Ber.*, 21, 1175).—The author has again obtained the isomeric methyloxyanthranol,



(*Abstr.*, 1881, 608), together with the ordinary form, in one experiment in which oxyanthranol was allowed to remain with aqueous soda and methyl iodide in a pressure flask for a week, and then heated for a day at a temperature gradually rising to 70°; but all experiments to determine the conditions of its formation have failed, since only traces, at the most, of the compound have been subsequently obtained. The colourless needles of the isomeride, which were separated mechanically from the yellow scales of methyloxyanthranol, melted at 98°, and were extremely soluble in benzene and light petroleum.

W. P. W.

Ethylated Hydroxyanthraquinones. By C. LIEBERMANN and G. JELLINEK (*Ber.*, 21, 1164—1171).—Liebermann and v. Kostanecki have stated that only those ethylated hydroxyanthraquinones which

contain two free hydroxyl-groups in the alizarin position can be mordanted on fabrics (*Annalen*, **240**, 245). In order to obtain evidence confirmatory of this theory, the authors have ethylated five of the hydroxyanthraquinones. It was not found possible to prepare tri-ethylated derivatives of anthrapurpurin, flavopurpurin, or anthragallol, although mono- and di-ethylated derivatives were readily obtained. In general it was found that ethylation proceeded the more rapidly the greater the number of hydroxyl-groups present, and the more these were grouped in contiguous positions in the formulæ of the compounds; moreover, with hydroxyanthraquinones containing three hydroxyl-groups in contiguous positions in their formulæ, it was found that the hydroxyl-group in the intermediate position was always ethylated first, although experiments with quinizarin and β -hydroxyanthraquinone showed that there was no perceptible difference in the ease with which hydroxyl-groups respectively in the α - and β -positions were displaced by ethoxyl. Spectroscopic observations showed that in solution in concentrated sulphuric acid, ethylated derivatives gave spectra closely resembling, and in some cases identical with those of the corresponding hydroxyanthraquinones.

Ethylation was effected in two ways, either by heating the hydroxyanthraquinone at 80° for some days in a reflux apparatus with dilute aqueous potash and an excess of ethyl iodide, or by heating the finely powdered hydroxyanthraquinone lead salt, dried at 120° , with a mixture of anhydrous benzene and ethyl iodide at 220° for 16 hours; the products obtained by the two methods were not always identical. The ethylated derivatives are very stable, and are not affected by boiling with ammonia, alkalis, or the ordinary solvents.

Ethoxyanthraquinone, $C_{14}H_7O_2 \cdot OEt$, forms yellowish-white needles.

Quinizarin ethyl ether, $OEt \cdot C_{14}H_6O_2 \cdot OH$, crystallises from alcohol in beautiful carmine needles, melts at 150 — 151° , forms a soluble barium salt, and is sparingly soluble in alkalis, yielding a red solution. The rose-red solution in sulphuric acid is fluorescent, as are the corresponding solutions of quinizarin and its diethyl ether; moreover, in passing from the former to the latter the colour of the solutions becomes more blue, just as is the case with eosin and its ethyl ether. *Quinizarin diethyl ether*, $C_{14}H_6O_2(OEt)_2$, crystallises in yellow needles and melts at 176 — 177° .

Anthragallol ethyl ether, $C_{14}H_5O_2(OH)_2 \cdot OEt$ [$OEt = 2$], prepared by the first method, crystallises from alcohol in small, red needles, melts at 175° , is soluble in hot alcohol, benzene, ether, and acetic acid, dissolves in concentrated sulphuric acid with an orange-yellow colour, and has no tinctorial powers. The *diethyl ether*, $C_{14}H_5O_2(OEt)_2 \cdot OH$, prepared by the first method, forms brown needles, melts at 134° , dissolves in concentrated sulphuric acid with an orange colour, and has no tinctorial powers. Prepared by the second method, *anthragallol ethyl ether* crystallises from alcohol in small, red needles, melts at 245° , is sparingly soluble in ether and alcohol, and dissolves in alkalis with a blue colour, yielding solutions which, unlike those of anthragallol, are not oxidised on exposure to air. It dissolves in concentrated sulphuric acid with a reddish-brown colour, and dyes mordanted fabrics. The *diethyl ether* prepared by the second method crystal-

lises from alcohol in silky, citron-yellow needles, melts at 198° , is readily soluble in ether and in hot alcohol, benzene, and acetic acid, dissolves in sulphuric acid with a reddish-yellow colour, and is destitute of tinctorial powers.

Anthrapurpurin ethyl ether, $C_{14}H_5O_2(OH)_2 \cdot OEt$, prepared by the first method, crystallises from alcohol in vitreous, orange-red needles, melts at 265° , is soluble in ether, &c., and dissolves in concentrated sulphuric acid with a reddish-violet colour. The *diethyl ether*, $C_{14}H_5O_2(OEt)_2 \cdot OH$, crystallises in matted, yellow needles, melts at 162° , is soluble in ether, &c., and dissolves in concentrated sulphuric acid with a reddish-violet colour. The *ethyl ether*, obtained as sole product by the second method, is deemed identical with that just described, although it crystallises in bright-yellow needles, melts at 170° , and gives a reddish-violet colour with concentrated sulphuric acid. These derivatives are destitute of tinctorial powers.

Flavopurpurin ethyl ether, $C_{14}H_5O_2(OH)_2 \cdot OEt$, is obtained in very small quantity by the first method, and is readily soluble in ether and alcohol. The *diethyl ether*, $C_{14}H_5O_2(OEt)_2 \cdot OH$, crystallises from dilute alcohol in long, hair-like, reddish-yellow needles, melts at 209° , is sparingly soluble in ether and alcohol, readily soluble in hot acetic acid, and dissolves in concentrated sulphuric acid with a blood-red colour. This derivative is the sole product obtained by the second method. These compounds have no tinctorial powers.

Rufigallol ethyl ether, $C_{14}H_5O_2(OH)_3 \cdot (OEt)_3$, prepared by the first method, crystallises in long, orange-red needles, melts at 195° , is sparingly soluble in alcohol, dissolves in concentrated sulphuric acid with a violet colour, and is destitute of tinctorial powers.

W. P. W.

Leuco-compounds from Anthraquinone Dyes. BY C. LIEBERMANN (*Ber.*, 21, 1172—1174; compare this vol., p. 492).—The method of simultaneously reducing and acetylating anthraquinone-derivatives by means of zinc-dust, sodium acetate, and acetic anhydride has been employed in the preparation of the following compounds:—

Diacetylhydroxyanthranol, $C_6H_4 \begin{array}{c} \diagup C(OAc) \\ | \\ \diagdown C(OAc) \end{array} C_6H_4$, obtained by the reduction of anthraquinone, crystallises from acetic acid in colourless needles, melts at 260° with decomposition, and is identical with the compound prepared by acetylating hydroxyanthranol (*Abstr.*, 1882, 855).

Diacetylmethylhydroxyanthranol, $C_6H_2 \cdot C_2(OAc)_2 \cdot C_6H_3Me$, prepared by the reduction of methylanthracene (m. p. = 177°), crystallises in scales melting at 217° .

Pentacetylhydroxyanthranol, $C_6H_4 \cdot C_2(OAc)_2 \cdot C_6H(OAc)_3$, formed by the reduction of anthragallol, crystallises from dilute alcohol in needles, and melts at 203° .

Tetracetylhydroxyanthranol, $OAc \cdot C_6H_3 \cdot C_2(OAc)_2 \cdot C_6H_3 \cdot OAc$, is obtained, together with a compound which is soluble in 50 per cent. alcohol, by the reduction of anthraflavic acid, and crystallises from acetic acid in silky needles melting at 274° .

Tetracetylhydroxyanthranol, $OAc \cdot C_6H_3 \cdot C_2(OAc)_2 \cdot C_6H_3 \cdot OAc$, forms
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one of two compounds obtained by the reduction of isoanthraflavic acid, and is separated by means of its sparing solubility in 50 per cent. acetic acid. It crystallises from alcohol in needles melting at 235—240°.

The more soluble products, which are simultaneously formed during the reduction-acetylation process, seem to be the corresponding peracetylated anthranols, and the yield of these is increased by increasing the duration of the reaction. Thus, flavopurpurin (this vol., p. 493) forms a pentacetylhydroxyanthranol as the chief product under the ordinary conditions, but when the reduction is continued for some time the proportions are reversed, and the tetracetyl-anthranol becomes the chief product. The tetracetyl-derivative melts not at 103—105°, but at 250—260°.

W. P. W.

Additive Derivatives of Dianthryl. By H. SACHSE (*Ber.*, **21**, 1183—1185).—*Dichlorodianthryl octochloride*, $C_{28}H_{16}Cl_2.Cl_8$, is obtained, together with a small quantity of dichloranthracene tetrachloride by treating a solution of dianthryl in chloroform with the calculated quantity of chlorine. It crystallises in white, microscopic scales, and is readily soluble in chloroform, benzene, and ether, and sparingly soluble in alcohol, acetic acid, and light petroleum, yielding non-fluorescent solutions which become fluorescent on heating owing to the decomposition of the compound. At 80°, it decomposes without previous fusion with the evolution of hydrogen chloride, and when heated with alcoholic potash for 1 to 2 hours is converted into *hexachlorodianthryl*, $C_{28}H_{12}Cl_6$. This crystallises in microscopic, greenish-yellow prisms, melts at 308—310°, and is readily soluble in benzene, sparingly soluble in alcohol and acetic acid, yielding fluorescent solutions.

Dibromodianthryl octobromide, $C_{28}H_{16}Br_2.Br_8$, is formed, together with a small quantity of dibromanthracene tetrabromide, when dianthryl is carefully treated with bromine in the cold. It crystallises in microscopic scales, melts at 156—160° with the evolution of bromine, is more stable than the octochloride, and dissolves readily in benzene and ether, but sparingly in alcohol and acetic acid, forming non-fluorescent solutions. When heated with alcoholic potash, a substitution-derivative, probably hexabromodianthryl, is obtained which crystallises in dark yellow prisms, melts at above 300°, and dissolves in acetic acid, yielding a fluorescent solution.

W. P. W.

Action of Acetic Acid on Citrene. By J. LAFONT (*J. Pharm.* [5], **17**, 105—108, 185—188).—Essence of citron, on fractional distillation, yields citrene, $C_{20}H_{16}$, as a principal product; this boils at about 178°, and has a rotatory power of $[\alpha]_D = +93^\circ$. When mixed with $1\frac{1}{2}$ vols. of glacial acetic acid, and heated on the water-bath for 48 hours out of contact with air, it is partly converted into an acetate, $C_{10}H_{16}.C_2H_4O_2$, which distils in a vacuum at 140—143°, has a sp. gr. of 0.9828 at 0°, and a rotatory power of $[\alpha]_D = +52^\circ 30'$; when saponified with alcoholic potash at 100°, a heavy viscous liquid, $C_{10}H_{16}.H_2O$, is obtained which distils at 126—128°, under a pressure of

40 mm., and has the distinct odour of hyacinth shown by List's terpinol. Its rotatory power is $[\alpha]_D = +67^\circ 30'$.

Citrene, when treated with formic acid in the cold during three months, affords some cymene and a compound, $C_{20}H_{32}$, which boils at 212° . This is a viscous, yellow substance with odour resembling that of copaiba, sp. gr. = 0.9404 at 0° ; it does not affect polarised light. Citrene and formic acid give the same products when heated at 100° in a sealed tube during 18 hours. J. T.

Terpinol. By G. BOUCHARDAT and R. VOIRY (*Compt. rend.*, 106, 663—665).—When terpinol, boiling at 172 — 176° (Abstr., 1887, 677), is saturated with hydrogen chloride at -25° , the oxygen compound, for which the authors propose the name *terpane*, is converted into the hydrochloride $2C_{10}H_{18}O.HCl$, whilst the terpinenic hydrocarbon forms the hydrochloride $C_{10}H_{16}.2HCl$. If the liquid is not cooled, the terpane is at once converted into the dihydrochloride. When the compound $(C_{10}H_{18}O)_2.HCl$ is washed with water at 0° , it is decomposed with development of heat and liberation of terpane. The hydrochloric acid is removed by treatment with dilute alkali, and the terpane is distilled under a pressure of 15 mm. at a temperature not exceeding 80° . The product boils at 78 — 79° in a vacuum, and is impure, but yields solid terpane if cooled to -50 — -55° ; the formation of crystals being accelerated by the addition of a fragment of the terpane from eucalyptol. This terpane boils at 174° , and its sp. gr. (0.935 at 0°) and melting point (-3° to -1°) are identical with those of terpane from eucalyptol and similar natural products. Its odour recalls that of menthol, &c. Hydrogen chloride converts it into the crystalline hydrochloride, $(C_{10}H_{18}O)_2.HCl$, which liquefies in a vacuum or under water with liberation of terpane. In a sealed tube, it decomposes spontaneously into $C_{10}H_{16}.2HCl$, $C_{18}H_{30}O$ and water. When treated with an ethereal solution of bromine, terpane yields a granular cinnabar-red product, which is a mixture of a red additive product with colourless substitution-derivatives; this reaction, like that with hydrochloric acid, may be used to separate terpane from terpinol but requires greater precautions. The terpane thus obtained always retains a small quantity of a hydrobromide of sp. gr. above 0.977, analogous to but more stable than the hydrochloride.

It follows from these reactions that List's terpinol consists of inactive crystalline terpinol or terpol, $C_{10}H_{16}O$, boiling at 218° ; terpane, $C_{10}H_{18}O$, boiling at 175° and crystallising at -1° ; and inactive terpinene, $C_{10}H_{16}$.

Terpane differs from active and inactive terpinenols in that it does not combine with acids or anhydrides to form ethereal salts. This confirms Wallach's observations, and supports his view that terpane is the ether or anhydride of terpene. C. H. B.

Oxidation of Hydrazocamphenes. By C. TANRET (*Compt. rend.*, 106, 660—662 and 749—751).—If a cold solution of α -hydrazocamphene in 1 per cent. sulphuric acid is gradually mixed with standard potassium permanganate solution until the colour just ceases to be discharged, it yields a blue precipitate of azocamphene,

$C_{10}H_{14}N_4O_8$. This is dissolved in ether, and the solution first washed with water and with dilute soda solution and then evaporated to dryness. Azocamphene thus obtained melts at 153° , and is insoluble in water but very soluble in cold ether, alcohol, and chloroform. A 50 per cent. ethereal solution gradually deposits a white crystalline powder which is insoluble in cold alcohol or ether but dissolves on heating with formation of a blue solution. The crystals become blue at 80° , and if kept at this temperature for some time regain their solubility in cold alcohol or ether. The white crystals have the same composition as the blue compound, melt at 153° , and are insoluble in cold water but dissolve in their own weight of chloroform, the solution becoming blue. It is evident that azocamphene can exist in two modifications, which the author distinguishes as *cyanazocamphene* and *leucazocamphene*. The azocamphene from β -hydrazocamphene exists only in the form of a blue resinous mass. Azocamphene is neutral to litmus and does not give with ferric chloride the violet coloration characteristic of the hydrazocamphenes.

At a temperature somewhat above its melting point, azocamphene decomposes with evolution of oxides of nitrogen. It also decomposes when heated with dilute acids or even with water, yielding hydrazocamphene and an acid, $C_{20}H_{32}N_2O_5$, which is somewhat resinous and is only slightly soluble in water, but dissolves in ether or chloroform. Its salts with alkalis and alkaline earths are soluble in water; the silver salt is only slightly soluble. Prolonged boiling with water decomposes it with production of a new acid which is insoluble in ether and has a high rotatory power.

Concentrated nitric acid acts very violently on the hydrazocamphenes, but the diluted acid yields the blue azocamphene, which, however, rapidly disappears. When the reaction has moderated, strong nitric acid is added, and the product is crystallised by concentration and converted into the calcium salt, which is recrystallised and then decomposed by hydrochloric acid. The *terebenthic acid*, $C_8H_{12}O_5$, thus obtained forms small anhydrous rhomboidal prisms, soluble in 8.2 parts of water at 14° and in 23 parts of ether, very soluble in alcohol, but insoluble in chloroform. It is optically inactive, melts at 164° , and at a higher temperature loses water, and then partially decomposes. When small quantities are distilled, a syrupy anhydride, soluble in chloroform, is obtained. When fused with potash, it decomposes above 240° with evolution of hydrogen and production of acetate, oxalate, and formate.

Terebenthic acid is bibasic, and the normal salts of the alkalis and alkaline earths are soluble and non-crystallisable. The acid ammonium salt forms slender needles soluble in eight parts of water. The acid calcium salt is only very slightly soluble and forms microscopic crystals. Neutral solutions of terebenthates give precipitates with solutions of silver, copper, lead, and iron (ferric), but no precipitates with solutions of zinc, cobalt, nickel, manganese, or mercury. The silver salt is granular, the copper salt is a blue-green powder. The normal zinc salt is soluble and non-crystallisable; when heated with water at 45° , it decomposes into a soluble acid salt, and a basic salt which is insoluble in the hot liquid but is partially decomposed when the

liquid cools, and yields a solution which, if concentrated, coagulates at 24° , but becomes limpid again when cooled.

Terebenthic acid is obtained from both α - and β -hydrazocamphene. Nitric acid also produces other acids less rich in carbon and not crystallisable.

Monohydrated sulphuric acid has no action on the hydrazocamphenes in the cold, but if the hydrazocamphene is treated at 200° with one-fifth its weight of acid it blackens, swells up, and evolves nitrogen and sulphurous anhydride. When the residue is treated with water and agitated with chloroform, it yields dihydrocamphines, $C_{20}H_{34}N_2O_4$, which are also formed, together with an alkaline carbonate and cyanide, when hydrazocamphenes are fused with potash.

Chromic acid converts hydrazocamphenes into neutral brown resinous products, insoluble in water, but soluble in alcohol, ether, and chloroform.

C. H. B.

Diterebenthyl. By A. RENARD (*Compt. rend.*, **106**, 856—858).—Diterebenthyl was allowed to fall drop by drop into an iron tube heated to incipient redness. Very little carbon was deposited, but some hydrogen, mixed with ethylene and propylene, was given off. The fraction of the product boiling below 70° contained amylene and hexylene, pentane, and hexane. The fraction at 70 — 78° contains hexine, and that at 100 — 110° consists chiefly of heptene. The most abundant fraction boils at 150 — 180° , and contains cymene and terebenthene hydrocarbons. It is evident that when decomposed by heat diterebenthyl yields practically the same product as terebenthene or essence of resin obtained by the distillation of colophony.

Bromine in carbon bisulphide forms the unstable derivative $C_{20}H_{30}Br_2$, which, when heated at 300° , yields diterebenthylene, a colourless, slightly fluorescent, thick oily liquid which boils at 345 — 350° ; sp. gr. at $12^{\circ} = 0.9821$; rotatory power for D in a column 1 cm. long = $+4^{\circ}$; vapour-density, 9.3. It does not alter when exposed to air, and is not affected by hydrogen chloride. Bromine yields the compound $C_{20}H_{24}Br_4$ as a deep-brown, amorphous mass. Well-cooled fuming nitric acid dissolves the hydrocarbon without evolution of nitrogen oxides, and on adding water the trinitro-derivative, $C_{20}H_{25}(NO_2)_3$, separates as a bulky, flocculent, yellow precipitate. Cold concentrated sulphuric acid has no action, but the hot acid or, better, the fuming acid, yields a sulphonic acid, $C_{20}H_{27}SO_3H$, distinguished from diterebenthylsulphonic acid by its greater mobility.

C. H. B.

Camphor Bases. By E. BAMBERGER (*Ber.*, **21**, 1125—1131).—In a previous paper the author has called attention to the analogy existing between the bases of the camphor-group and β -tetrahydronaphthylamine (this vol., p. 159). This is well shown in the case of bornylamine, which, like β -tetrahydronaphthylamine, has a peculiar piperidine-like odour, is strongly alkaline, and reacts with diazobenzene chloride to yield an oil having properties similar to those of diazoamidotetrahydro- β -naphthylamine (compare this vol., p. 712). Bornylamine nitrate is not decomposed by prolonged boiling with

water, and noteworthy quantities escape decomposition when a 10 per cent. aqueous solution is heated at 130° for four hours. Finally, just as β -tetrahydronaphthylamine decomposes into naphthalene, ammonia, and hydrogen (*loc. cit.*), so bornylamine seems to yield ammonia and either camphor or its decomposition products. On these grounds, the author considers that bornylamine is a tetrahydro-derivative of an aromatic base, and is probably tetrahydrocarvacrylamine. From this it follows that camphor, which yields bornylamine on treatment with ammonium formate (Leuckart and Bach, *Abstr.*, 1887, 376), a reaction involving, as Leuckart has shown, the displacement of the oxygen present in the carbonyl-group by hydrogen and the amido-group, is a ketotetrahydrocymene [$\text{Pr} : \text{O} : \text{Me} = 1 : 3 : 4$].

Camphylamine, which Leuckart (*loc. cit.*) regards as a position-isomeride of bornylamine, differs from the latter, since it has the properties of a fatty amine, and yields a hydroxy-derivative in the usual way. The remainder of the paper is devoted to a discussion of the probable formulæ of the anhydride of camphoroxime.

W. P. W.

Lactucerin. By O. HESSE (*Annalen*, **244**, 268—273).—The melting point of pure α -lactuceryl varies. If the temperature is slowly raised it melts at 173°, but if it is rapidly heated it melts at 181°. The *diacetate*, prepared by boiling a mixture of lactuceryl with acetic anhydride crystallises in plates and melts at 198—200°. The *monacetate* melts between 202° and 207°. The *dibenzoate* is freely soluble in ether, chloroform, and light petroleum. It melts at 156°.

W. C. W.

Apiole. By J. GINSBERG (*Ber.*, **21**, 1192—1194).—When apiole is boiled with alcoholic potash, a compound is obtained, which crystallises in satiny scales, and has the same percentage composition as apiole (compare v. Gerichten, this Journal, 1876, ii, 533). On oxidation with nitric acid (sp. gr. = 1.48), apiole yields oxalic acid and a *nitro*-compound. This crystallises in lustrous, golden needles, melts at 116°, and on reduction with stannous chloride and alcoholic hydrogen chloride is converted into a *base*, which crystallises from water in long, yellow needles, melts at 118°, dissolves in mineral acids with a red colour, and gives with ferric chloride a violet coloration rapidly changing to blood-red. The *picrate* of the base crystallises in small, brown scales; the *hydrochloride* is an indistinctly crystalline powder, and the *acetyl*-derivative crystallises in colourless scales, melts at 260°, and is sparingly soluble in cold alcohol and ether.

W. P. W.

Emodin in Nephroma Lusitanica. By E. BACHMANN (*Chem. Centr.*, 1888, 47, from *Ber. deut. Bot. Ges.*, **5**, 192—194).—The colouring matter obtained from this lichen behaves towards alkalis like crysophanic acid, but differs from the latter in being readily soluble in alcohol, glacial acetic acid, and amyl alcohol. The colouring matter agrees most closely with emodin, a substance first found in rhubarb, and occurring also in the bark and berries of *Rhamnus frangula*.

J. P. L.

Chlorophyll. By J. WOLLHEIM (*Ann. Agronom.*, **14**, 141—143, from *Bot. Centr.*, **32**, 310).—The author, who has been studying this substance both spectroscopically and chemically for some time past, gives the following preliminary notice of his results:—

The fresh solution in absolute alcohol is fluorescent, whilst the colouring matter in the fresh leaf is not. The absorption-bands are the same in relative intensity, but are narrower, and a little displaced towards the blue end of the spectrum. Fuming hydrochloric and sulphuric acids give non-fluorescent solutions with absorption-bands exactly like those of the fresh leaf. It is therefore evident that the colouring matter is changed by the action of alcohol. On adding water to the acid solutions, or weak acids to the alcoholic solution, a greenish-brown precipitate is obtained, soluble in alcohol, ether, chloroform, and benzene, giving the first two bands like the fresh tincture, the band III more feeble, IV stronger, and in addition a fifth band between $\lambda = 491$ and $\lambda = 509$, which has already been observed in the fresh leaf, but which appears to belong to a second absorbing substance. Fresh leaves treated with alkalis give fluorescent solutions with absorption-bands still more displaced towards the blue, and also the band III feebler and IV stronger than in the tincture. When the alkaline solution is gently heated, the bands are restored to their normal intensity, and the fluorescence disappears, but the displacement of the bands persists. When the greenish-brown precipitate (chlorophyllane) is dissolved in pure hydrochloric acid, the green solution (Frémy's phyllocyanin) again gives the spectrum of the fresh tincture. It seems, therefore, that certain atoms combined during the formation of chlorophyllane, and causing the reinforcement of band IV, are removed or substituted under the influence of hydrochloric acid. Water gives with this solution another precipitate (phyllocyanic acid), whose alcoholic solution shows a strong band IV. This suggests the entrance of hydroxyl into the combination. The spectrum of phyllocyanic acid is identical with that of chlorophyllane. The precipitate, redissolved and reprecipitated many times, washed, and taken up by chloroform, may be obtained in crystals; after many crystallisations these contain no iron or mineral matter, and give on analysis numbers corresponding with the formula $C_{26}H_{47}N_3O_6$. Phyllocyanic acid is a compound with a fatty substance. Its ammoniacal solution being precipitated with lead acetate, the precipitate extracted with alcohol, and the green alcoholic solution decomposed with hydrogen sulphide, the reddish-brown substance is left in the alcoholic solution, which is fluorescent, and gives the spectrum of chlorophyllane; whilst the band V has disappeared, showing that it belonged to the fatty substance precipitated by the lead salt. The fatty substance, whose spectrum coincides with that of xanthophyll, is no other than cholesterin. The red-brown substance thus freed from cholesterin is called by the author phyllorubin, and has the properties of an alcohol. On oxidation it behaves exactly like the bilirubin of the bile, becoming in succession blue, violet, red, and yellow. Oxidised with precaution, it yields an acid, whose copper salt shows the same displacement of absorption-bands towards the blue as alkaline chlorophyll. This copper salt is easily formed, and is the substance that gives the fine

blue-green non-fluorescent colour to vegetable preparations made in copper vessels.

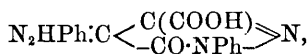
When phyllorubin is dissolved in chloroform and treated with a current of dry hydrogen chloride, phyllocyanin is first formed (giving the same spectrum as the alcoholic tincture of chlorophyll), and afterwards a greenish-blue colouring matter, the spectrum of which is identical with that of the fresh leaf. The same substance is formed by treating phyllorubin with other dehydrating reagents, such as sulphuric and phosphoric acids. It should therefore be considered as an ether (hydroxy-derivative?). It separates from the chloroform solution in crystalline plates with metallic lustre, and its behaviour with reagents is the same as that of chlorophyll. The chloroform solution is non-fluorescent, but either alcohol or glycerol gives a fluorescent solution with displaced spectrum.

J. M. H. M.

Identity of Phenylmethylpyrazoloneazobenzene with Phenylhydrazineketophenylmethylpyrazolone: Inner Anhydride Formation of Diphenylhydrazineacetylgyoxylic Acid and Diphenylhydrazinedihydroxytartaric Acid. By L. KNORR (*Ber.*, 21, 1201—1205).—Phenylmethylpyrazoloneazobenzene (*Abstr.*, 1887, 602) is identical with phenylhydrazinephenylmethylketopyrazolone (*ibid.*, 603). Both compounds melt at 155°; they crystallise from hot alcohol in orange-red, shining needles, which dissolve in hot dilute soda, forming a deep yellow solution, from which they are precipitated in the form of the sodium salt by the addition of strong soda. When the alkaline solution of either compound is acidified, the original substance, melting at 155°, is obtained. On warming a nitric acid solution of either compound, the whole suddenly solidifies to a mass of fine, yellow needles. This new substance is *phenylmethylketopyrazolonehydrazone*, $N_2HPh \cdot C \begin{smallmatrix} < -CMe:N \\ -CO \cdot NPh \end{smallmatrix} >$. Its solubility in

soda is probably owing to the formation of the sodium salt of diphenylhydrazineacetylgyoxylic acid, and on acidifying the free acid is converted into the inner anhydride. Similarly, on acidifying, an alkaline solution of the osazone of acetylgyoxylic acid (*loc. cit.*), the inner anhydride phenylhydrazinephenylmethylketopyrazolone is obtained.

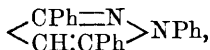
Diphenylhydrazinedehydroxytartaric acid (Ziegler and Locher, *Abstr.*, 1887, 578) is converted into the inner anhydride when its alkaline solution is poured into acetic acid, or when the acid is crystallised from acetic acid. This anhydride,



phenylhydrazineketophenylpyrazolonecarboxylic acid, melts at 230—232°, and loses 1 mol. of carbonic anhydride when carefully heated at 230°; a brown oil is thus obtained, which solidifies on cooling, and yields brown-yellow crystals, melting at 150° after recrystallisation from alcohol. This compound is probably phenylhydrazineketophenylpyrazolone, $N_2HPh \cdot C \begin{smallmatrix} < CH=N \\ -CO \cdot NPh \end{smallmatrix} >$; on heating a few degrees above 230°, it is completely decomposed. The same substance appears to be

formed by boiling the osazone of glyoxalcarboxylic acid (Nastvogel, *Inaug. Diss.*, Würzburg, 1887) with acetic anhydride. F. S. K.

Pyrazoles and Pyrazolines. By L. KNORR and H. LAUBMANN (*Ber.*, 21, 1205—1212).—1.3.5-Triphenylpyrazole,



is obtained by warming dibenzoylmethane with an excess of phenylhydrazine. It crystallises from ether in large, well-defined plates, melting at 137—138°, and from dilute alcohol in leaflets which contain varying quantities of alcohol, according to the concentration of the solution, and yield the pure pyrazole when gently heated. It is insoluble in water and dilute acids, sparingly soluble in cold ether and alcohol, but dissolves readily in hot alcohol or ether, in chloroform, benzene, and glacial acetic acid. Triphenylpyrazole has only a feebly basic character, and is completely precipitated from its solution in concentrated sulphuric or nitric acid by the addition of water. It remains unchanged when heated with 20 per cent. hydrochloric acid at about 300°.

Triphenylpyrazole methiodide, $\text{C}_{22}\text{H}_{19}\text{N}_2\text{I}$, is formed when the pyrazole is heated with an excess of methyl iodide and methyl alcohol at 110°. It forms white needles, which melt at 176° with decomposition, and are sparingly soluble in cold, more readily in warm water. It dissolves in alcohol and chloroform, but is insoluble in alkalis, ether, and benzene. When heated, it yields methyl iodide and triphenylpyrazole.

Triphenylmethylpyrazine, $\begin{array}{c} \text{CHPh}\cdot\text{NMe} \\ \text{CH}_2\cdot\text{CHPh} \end{array} \text{NPh}$, is produced by the action of sodium on a boiling alcoholic solution of the preceding compound. It melts at 109—110° or when placed in boiling water; it is insoluble in water, and only sparingly soluble in cold alcohol and light petroleum, but dissolves readily in hot alcohol, ether, and benzene, the solutions showing a slight blue fluorescence. This compound does not show the reactions of pyrazolines, and it yields a brown resinous product when treated with concentrated nitric acid.

Bromotriphenylpyrazole, $\text{C}_{21}\text{H}_{15}\text{N}_2\text{Br}$, is obtained by treating a chloroform solution of the pyrazole with bromine. It crystallises from alcohol in white, shining, silky needles, which melt at 142°, and dissolve readily in ether, benzene, and hot alcohol, but are insoluble in water and dilute acids. It does not lose bromine when treated with aqueous or alcoholic potash.

Nitrosotriphenylpyrazole, $\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}$, is formed when nitrous acid is passed into an ethereal solution of the pyrazole. It crystallises in green needles, which melt at 183°, are sparingly soluble in ether and light petroleum, but dissolve readily in benzene and chloroform. An aqueous or sulphuric acid solution of nitrous acid does not act on triphenylpyrazole.

1.3.5-Triphenylpyrazoline, $\begin{array}{c} \text{CPh}=\text{N} \\ \text{CH}_2\cdot\text{CHPh} \end{array} \text{NPh}$, is obtained by re-

ducing triphenylpyrazole with sodium and alcohol, or by warming an alcoholic solution of benzalacetophenone with phenylhydrazine. It crystallises in needles, melting at 134—135°, dissolves readily in ether, benzene, hot alcohol, and glacial acetic acid, with blue fluorescence, but is insoluble in water and dilute acids. It is only acted on at 300° by a 20 per cent. solution of hydrochloric acid, and a solution of this compound in sulphuric acid is turned blue-green by a drop of a nitrite solution. Triphenylpyrazole is formed when gaseous nitrous acid is passed into an ethereal solution of this compound until the blue fluorescence disappears; if the gas is passed for a longer time, the yellow solution becomes deep green, and nitrosotriphenylpyrazole (see above) is obtained; when, however, the triphenylpyrazoline is just covered with a small quantity of ether and nitrous acid passed, a brownish-yellow, indifferent substance is produced. This compound is insoluble in water, acids, and alkalis, and dissolves very sparingly in alcohol and ether; it is, however, readily soluble in chloroform and benzene, and crystallises from glacial acetic acid in forms melting at 175—176°. It appears to be *nitrotriphenylpyrazoline*, $C_{21}H_{17}N_3O_2$. The same compound, together with triphenylpyrazole, is produced when triphenylpyrazoline, in ethereal solution, is oxidised with nitric acid.

Triphenylpyrazoline tribromide, $C_{21}H_{15}N_2Br_3$, is obtained by treating a chloroform solution of triphenylpyrazoline with bromine. It crystallises from ether, alcohol, or light petroleum, in small needles, melting at 179°, and is reconverted into the pyrazoline by nascent hydrogen. F. S. K.

1.5-Diphenylpyrazoline. By H. LAUBMANN (*Ber.*, **21**, 1212—1213).—1.5-*Diphenylpyrazoline*, $C_{15}H_{14}N_2$, can be obtained by distilling the hydrazine of cinnamaldehyde (Fischer, *Abstr.*, 1884, 1151). It crystallises from alcohol or light petroleum in shining, silky needles, melting at 137—138°. It is insoluble in water, sparingly soluble in light petroleum, dissolves more readily in alcohol, and readily in ether, benzene, and chloroform, the solutions showing a slight blue fluorescence. It gives a pyrazoline reaction similar to that shown by methyl-diphenylpyrazoline (Knorr and Blank, *Abstr.*, 1885, 506). Acid solutions of this compound are coloured magenta by oxidising agents. F. S. K.

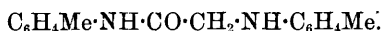
Decomposition of Anilides at a High Temperature. By C. A. BISCHOFF (*Ber.*, **21**, 1257—1265; compare *Abstr.*, 1883, 919).—

Diphenyldiketopiperazine, $PhN<\begin{smallmatrix} CO\cdot CH_2 \\ CH_2\cdot CO \end{smallmatrix}>NPh$, is obtained by the action of aniline on chloracetic acid or ethyl chloracetate.

Phenylglycinphenylamidacetic acid, $NHPh\cdot CH_2\cdot CO\cdot NPh\cdot CH_2\cdot COOH$, and *methylphenylglycinanilide*, $NHPh\cdot CH_2\cdot CO\cdot NPhMe$, are also produced by acting on chloracetic acid with aniline. The former compound is also formed when diphenyldiketopiperazine is boiled with strong acids or alkalis.

Paratoluidine chloracetate, $C_6H_4Me\cdot NH_2\cdot O\cdot CO\cdot CH_2Cl$, forms colourless crystals, which melt at 97.5° and are readily soluble in alcohol and ether.

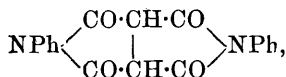
Paraditolylldiketopiperazine, $C_6H_4Me \cdot N < \begin{smallmatrix} CO \cdot CH_2 \\ CH_2 \cdot CO \end{smallmatrix} > NC_6H_4Me$, is produced when the preceding compound is heated; it can also be obtained from ethyl monochloracetate and *paratolylglycintoluide*,



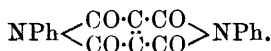
The last-named compound crystallises from hot alcohol in leafy forms which melt at 134° .

Orthotoluidine chloracetate, $C_6H_4NO_2Cl$, melts at 95° , dissolves readily in alcohol and warm water, less readily in ether.

Orthoditolylldiketopiperazine is obtained from toluidine and chloracetic acid or ethyl chloracetate. By heating aniline with malic acid, a compound, $PhN < \begin{smallmatrix} CO \cdot CH : CH \cdot CO \\ CO \cdot CH : CH \cdot CO \end{smallmatrix} > NPh$, is produced. Similarly ethyl acetylenetetra-carboxylic acid yields a compound,



and ethyl dicarbintetra-carboxylic acid gives a compound,



The above compounds will be more fully described in a future publication. F. S. K.

Pyridine Bases from Coal-tar. By J. MOHLER (*Ber.*, **21**, 1006—1015).—The existence of a pyridine hydrate, $C_5NH_5 \cdot 3H_2O$, seems to be confirmed by the author's experiments. β -Picoline was isolated from a mixture of coal-tar bases, and symmetrical collidine was obtained from the same source by fractional precipitation with potassium ferrocyanide.

Collidine from coal-tar is a colourless liquid which does not change on exposure to the air. It dissolves slowly but to a considerable extent in cold water, and separates again almost quantitatively on warming. The *mercurochloride*, $C_5H_2Me_3N \cdot HCl \cdot 2HgCl_2$, crystallises in prisms melting at 155° , and is only sparingly soluble in water. The *aurochloride*, $C_5H_{11}N \cdot HAuCl_4$, forms long, yellow needles which become brittle and dull on exposure to the air; the dry salt melts at 114 — 115° , but when heated under water it changes to an oil at a lower temperature. The *dichromate*, $(C_5H_{11}N)_2 \cdot H_2Cr_2O_7$, crystallises from water in long, yellow prisms which decompose at 190° , and are sensitive to light, becoming greyish-yellow coloured in the sunlight. The *picrate* crystallises in long, silky needles melting at 155 — 156° . The sulphate, nitrate, and hydrochloride are not deliquescent. The *hydrochloride* forms slender needles which sublime, with partial decomposition, without melting. The *sulphate* forms transparent prisms melting at 203° . The *nitrate* crystallises in hexagonal leaves which melt above 300° with decomposition.

Pyridine ferrocyanide, $(C_5H_5N)_2 \cdot H_4Fe(CN)_6 + 2H_2O$, forms monoclinic prisms in combination with domes; it is more sparingly soluble

in water than the ferrocyanides of the homologous bases, and can be employed as a means of obtaining pure pyridine. The ferrocyanides of the picolines are very readily soluble, that of $\alpha\alpha'$ - and of $\alpha\gamma$ -lutidine are more sparingly soluble. The aqueous solutions of the ferrocyanides are tolerably stable in the cold, but decompose when heated above 70° .
F. S. K.

Distillation of Salts of Pyridinecarboxylic Acids. By F. BLAU (*Ber.*, 21, 1077—1078).—On dry distillation, the copper salt of picolinic acid yields an oil from which a strong base, probably $\alpha\alpha$ -dipyridyl, was isolated. This compound separates from water in crystals which melt at 70° ; it is sparingly soluble in water, but dissolves readily in other solvents.
F. S. K.

Amide of Dihydroxyisonicotinic Acid. By S. RUHEMANN (*Ber.*, 21, 1247—1249).—Trichlorocitrazinamide (this vol., p. 255) combines with aniline to form a compound, $C_{18}H_{14}N_4O_3$, which is a strong base, and dissolves very readily in hydrochloric acid; it has also feebly basic properties and dissolves in ammonia. It is very sparingly soluble in alcohol, and is decomposed when boiled with glacial acetic acid.

A crystalline product, $C_6H_4N_2O_3$, is obtained by heating a hydrochloric acid solution of the preceding compound. This substance has acid properties and dissolves in ammonia, forming a yellow solution; it decomposes on heating, and its aqueous solution is turned deep brown by ferric chloride. Silver nitrate precipitates from an ammoniacal solution a yellow, gelatinous precipitate which blackens on heating. Heated with potash, ammonia is evolved, and a salt formed which is soluble in ether.
F. S. K.

Quinolinesulphonic Acids. By A. CLAUS (*J. pr. Chem.* [2], 37, 258—268; compare Abstr., 1887, 737, and this vol., pp. 296 and 501).—When quinoline is sulphonated with fuming sulphuric acid containing from 10 to 20 per cent. of anhydride at a temperature not exceeding 125 — 130° , three sulphonic acids are formed: the meta-, the ortho-, and an acid belonging to the ana-series. At a temperature of between 170 — 180° only the last two are obtained. These facts explain the contradictory statements of La Coste and Valeur, and Fisher, Bedall, and Riemerschmied. The three acids may be best separated by the fractional crystallisation either of the free acids or of their barium or calcium salts. The meta-acid (4 mols. H_2O) is the most soluble, and crystallises in small colourless needles. The potassium ($1\frac{1}{2}$ —2 mols. H_2O) and sodium (3 mols. H_2O) salts are both somewhat hygroscopic. The calcium salt (4 mols. H_2O) crystallises from water in microscopic needles; the barium salt (4 mols. H_2O) is only indistinctly crystalline. The silver, lead, and copper salts are described. The sulphochloride forms a sticky mass, and the sulphonamide an indistinctly crystalline powder melting at 119° (uncorr.). On heating the silver salt with ethyl iodide in sealed tubes at 140° , the ethyl salt $C_8NH_5\cdot SO_3Et$ is formed. It melts at 275° (uncorr.).

When quinolinemetasulphonic acid is treated with bromine in the

cold, additive products of little stability are formed; whilst at the temperature of the water-bath, the sulphonic group is displaced by bromine. A dibromoquinoline which sublimes in needles melting at 255° , and a tribromoquinoline melting at 199° , have been thus obtained.

Quinolinemetasulphonic acid when fused with potash yields a *hydroxyquinoline*, which softens at 165° and melts below 200° ; whilst the ana-compound prepared synthetically from amidobenzenemetasulphonic acid yields an *hydroxyquinoline*, melting sharply at 224° (uncorr.).

Sodium quinolineorthosulphonate crystallises in needles with 5 mols. H_2O , the potassium salt with 2 mols. H_2O , and the copper salt in small green needles with 2 mols. H_2O . The lead salt is anhydrous.

Quinolineorthosulphonic acid cannot be directly brominated, but bromoquinolineorthosulphonic acid may be obtained by heating ethyl orthoquinolinesulphonate with bromine in sealed tubes at 180° . It decomposes at 350° without previously melting. The sodium salt (1 mol. H_2O) crystallises in needles; the lead, silver, and potassium salts are anhydrous. The copper salt (2 mols. H_2O) forms dark-green prisms. The sulphochloride melts at 88° , the sulphonamide at 185° , and the ethyl salt, $C_9H_5BrNSO_3Et$, at 98° .

On treating an aqueous solution of bromoquinolineorthosulphonic acid with bromine, a new *tribromoquinoline* crystallising in yellow prisms and melting at 205° is obtained. G. T. M.

Cinchoniline. By E. JUNGLEISCH and E. LÉGER (*Compt. rend.*, 106, 657—660).—*Cinchoniline*, $C_{19}H_{22}N_2O$, is obtained by treating the dihydriodide (this vol., pp. 380 and 507) with sodium hydroxide, which is then agitated with ether. The ethereal solution is washed with water and concentrated, when it deposits bulky, yellowish crystals, which are purified by recrystallisation. Cinchoniline crystallises more readily than its isomerides, and forms very large, colourless, anhydrous, right rhomboidal prisms. It melts without decomposition at 130.4° , and distils in a vacuum without undergoing rapid alteration; rotatory power of a 1 per cent. solution in alcohol of 97° at 75° $[\alpha]_D = +53.22^{\circ}$; in $\frac{1}{2}$ a per cent. solution $[\alpha]_D = +50.3^{\circ}$. In a 1 per cent. solution in dilute hydrochloric acid containing 2 mols. HCl for each molecule of base $[\alpha]_D = +59.15^{\circ}$; if 4 mols. HCl $[\alpha]_D = +63.10^{\circ}$. The base is only slightly soluble in water, but the solution is strongly alkaline to litmus and phenolphthalein. It dissolves readily in ethyl and methyl alcohols, chloroform, benzene, ether, and acetone. It reduces potassium permanganate in the cold, and when decomposed by heat yields the same products as cinchonine.

Cinchoniline forms basic salts which are feebly alkaline to litmus and normal salts which have no acid reaction; the majority of the salts are very soluble in water, and have a remarkable power of forming large crystals. The *basic hydrochloride*, $C_{19}H_{22}N_2O \cdot HCl$, is extremely soluble even in cold water, but crystallises from the syrupy solution in very large, oblique, rhomboidal prisms which melt with decomposition at 226° . In an aqueous solution containing 1 per cent., $[\alpha]_D = +5.0^{\circ}$

at 16°. The *platinochloride* forms small, orange-yellow prisms containing 1 mol. H_2O ; the *aurochloride*, $(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}, 2\text{HCl}, \text{AuCl}_3)_2 + \text{H}_2\text{O}$, crystallises in small, bright yellow, highly refractive prisms. The *basic hydrobromide*, $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}, \text{HBr} + 3\text{H}_2\text{O}$, is much less soluble than the basic hydrochloride, and forms long prisms which melt with decomposition at about 228°. The *basic hydriodide* is very soluble in water, and forms short, colourless prisms containing 1 mol. H_2O . It melts with decomposition at about 221°. The *normal hydriodide*, obtained by adding an alkaline iodide to a normal cinchoniline salt, forms short, hard, bright yellow anhydrous prisms, insoluble in water containing hydriodic acid. The *basic thiocyanate*,



forms long, silky, efflorescent needles only slightly soluble in cold water; the *basic chromate* forms an oily precipitate; the *basic oxalate* is extremely soluble, and crystallises in large prisms; the *normal oxalate* is likewise very soluble, and crystallises in needles; the *normal picrate* is amorphous.

Cinchoniline methiodide, $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}, \text{MeI}$, obtained by the action of methyl iodide on the base in presence of anhydrous ether, crystallises from alcohol in short, highly refractive prisms, and from water in long, colourless prisms. Both forms are anhydrous and melt with decomposition at about 233°. The *ethiodide*, obtained in a similar manner, crystallises from water or alcohol in highly refractive prisms containing 1 mol. H_2O . It is very soluble in water, alcohol, and chloroform, but is insoluble in benzene or ether. *Cinchoniline ethobromide* forms hard crystals, and is soluble in alcohol, but insoluble in ether.

C. H. B.

Ptomaïnes. By O. DE CONINCK (*Compt. rend.*, **106**, 858—861).—The flesh of cuttle fish, with the sepia bags removed, was allowed to putrefy, and the alkaloids were extracted by Gautier's process. Several of the ptomaïnes described by Brieger were obtained, and two others of the composition $\text{C}_8\text{H}_{11}\text{N}$ and $\text{C}_{10}\text{H}_{15}\text{N}$ respectively.

The alkaloid $\text{C}_8\text{H}_{11}\text{N}$ is a somewhat mobile, yellowish, strongly smelling liquid, very soluble in water, and also readily soluble in methyl or ethyl alcohol, ether, and acetone. When dry, it boils without decomposition at 202°; sp. gr. at 0° = 0.9865. When exposed to air, it becomes brown and absorbs moisture, and then boils at a lower temperature. The *hydrochloride*, $\text{C}_8\text{H}_{11}\text{N}, \text{HCl}$, forms deliquescent, white or yellowish radiating masses, very soluble in water at all temperatures. The *hydrobromide* is similar, but is less deliquescent and less soluble. The *platinochloride*, $(\text{C}_8\text{H}_{11}\text{N})_2, \text{H}_2\text{PtCl}_6$, is deep yellow and almost insoluble in cold water, but soluble in hot water. It is somewhat stable, but decomposes more readily than the platinochlorides of the pyridine bases. Water at 80° or 100° decomposes it with formation of a pale brown powder $(\text{C}_8\text{H}_{11}\text{N})_2, \text{PtCl}_4$, insoluble in cold water, and almost insoluble in hot water. The *aurochloride* is pale yellow, and is somewhat stable in the cold, but decomposes on heating.

The salts of this ptomaïne are less stable than those of the pyridine

bases, and more closely resemble the salts of hydropyridines. If a cold solution of the hydrochloride is mixed with excess of gold chloride, some gold is reduced. C. H. B.

Ptomaines. By I. GUARESCHI (*Chem. Centr.*, 1888, 45, from *Ann. Chim. Farm.*, 87, 237—249).—The author has made some experiments with the object of excluding, if possible, the objection that has been urged with regard to these bases, namely, that they may not pre-exist, but arise from the action of the reagents (acid, alcohol, &c.) used in their extraction. From putrid fibrin, he has obtained a very satisfactory yield of a base, $C_{10}H_{13}N$, previously described by him, by making the mass alkaline with baryta in the cold, and extracting with ether and chloroform. This base pre-exists in the putrid fibrin. From the chloroform extract, another compound, $C_{14}H_{20}N_2O_4$, which appears to be an amido-acid, was obtained. It forms beautiful, shining plates melting at $248-250^\circ$, soluble in water and alcohol, but not readily soluble in chloroform. The watery solution is neutral or feebly acid, and gives all the general alkaloid reactions. When a weak hydrochloric acid solution of the base is precipitated with platinum chloride, the platinochloride of the base $C_{10}H_{13}N$ is formed. J. P. L.

A Cadaveric Alkaloid behaving like Strychnine. By C. AMTHOR (*Chem. Centr.*, 1888, 43, from *Chem. Zeit.*, 11, 288).—An alkaloid with strychnine-like properties has twice been obtained from parts of a corpse eight days old.

The chief differences between this alkaloid and strychnine are:—(1) It is less poisonous than strychnine when injected subcutaneously in the frog; (2) from alkaline solutions, ether dissolves but a very small quantity, whereas amyl alcohol dissolves it easily; (3) the taste is less bitter; (4) the precipitates with potassium ferrocyanide and ferricyanide, potassium chromate and picric acid are amorphous, those of strychnine crystalline; (5) the blue colour with potassium chromate and sulphuric acid is less persistent and less pure than the colour formed with strychnine. J. P. L.

Hæmoglobin of Dog's Blood. A. JAQUET (*Zeit. physiol. Chem.*, 12, 285—288).—Hæmoglobin was prepared from dog's blood, according to the method adopted by Zinoffsky (*Abstr.*, 1886, 165) in the case of horse's blood, and then twice recrystallised. Elementary analysis gave the following percentage results, which for the sake of comparison are placed side by side with the numbers obtained by Zinoffsky:—

	Hæmoglobin of dog.	Hæmoglobin of horse (Zinoffsky).
C.....	53.91	51.15
H.....	6.62	6.76
N.....	15.98	17.94
S.....	0.542	0.390
Fe.....	0.333	0.335
O.....	22.62	23.43

W. D. H.

Action of Alloxantin on Blood. By N. KOWALEWSKI (*Chem. Centr.*, 1887, 1296, from *Med. Centr.*, **25**, 658—659, 676—678).—The author refers to a former paper (*Abstr.*, 1887, 508) regarding the change into methæmoglobin that hydroxyhæmoglobin undergoes by the action of alloxantin, and shows in several instances how this change may take place under the influence of reducing agents. By the action of alloxantin on blood, the former reduces the oxyhæmoglobin to hæmoglobin, and is oxidised itself to such compounds as are able to change the reduced hæmoglobin into methæmoglobin. J. W. L.

Physiological Chemistry.

Chemistry of Fish; Analysis of American Specimens. By W. O. ATWATER (*Amer. Chem. J.*, 10, 1—20; compare this vol., p. 308).—Tables are given of the composition of the flesh of fish, showing matters extracted by cold water and not coagulated; albumin coagulated from cold water extract; gelatin extracted by hot water; insoluble protein; fats, ash, and water; also tables showing the amounts of phosphoric, sulphuric, and hydrochloric acids in the ash. From these data, tables are constructed showing the relative value of various fish as foods. Analyses are also given of fresh and whole fish, and of salted and cured, or canned fish. H. B.

Occurrence of Fluorine in the Organism. By G. TAMMANN (*Zeit. physiol. Chem.*, 12, 322—326).—The method adopted for the quantitative estimation of fluorine was as follows:—The substance under investigation was treated with powdered quartz and sulphuric acid. A current of dry air carried the silicon fluoride so formed through a narrow tube where it was decomposed with steam and the silicic acid collected on the walls of the tube, hydrofluosilicic acid being also formed; the latter was absorbed in aqueous potash, and evaporated to dryness; the residue was taken up with hydrochloric acid, the potassium silicofluoride precipitated with alcohol, filtered, and titrated with potassium hydroxide solution. Fluorine is well known to be a constant constituent of bone; it is also known to occur in ploughed earth and in wells. Horsford (*Annalen*, 149, 202) found weighable quantities of fluorine in the human brain, and Salm-Horstman (*Ann. Phys. Chem.* 114, 510) found that certain plants did not fully develop in the absence of fluorine.

In the present research, plants grown in culture liquids which did not contain fluorine, were found to die quickly when fluorine was added to such liquids; thus, the addition of 0.1 gram of potassium fluoride per litre caused death in these plants in 12 hours.

The different parts of the egg were investigated; the shell contained imponderable traces only; the white contained somewhat larger traces, but still imponderable; the yolk yielded weighable quantities; 84 grams of fresh yolk contained 0.0009 gram of fluorine. Attention

is drawn to the fact that the brain and egg-yolk, tissues that contain much phosphorus, are also richest in fluorine. In other experiments, brain, cow's milk, and blood were found to contain small weighable quantities of fluorine.

From these experiments, certain conclusions are drawn, the chief purport of which is, that fluorine is of greater physiological importance in the animal economy than has hitherto been considered to be the case.

W. D. H.

Digestion of Albumin. By J. BOAS (*Chem. Centr.*, 1887, 1226, from *Zeit. Klin. Med.*, 12, 231).—A comparative study of the three chief products, syntonin, hemialbumose, and peptone, of the artificial and natural digestion of albumin has been made. In artificial digestion, syntonin is formed at a very early stage with all the three kinds of albumin experimented on (fibrin, egg albumin, and scraped meat); the amount formed, however, varies considerably.

Hemialbumose is a constant product of fibrin digestion and a frequent product, though in much smaller quantity, of egg albumin digestion; it is altogether absent in the digestion of meat. Hemialbumose must be regarded more as a bye-product of digestion than as an intermediate step in the process, for, like syntonin, it is a product of the action of acid. Any hemialbumose formed is gradually converted into peptone, so that after long prolonged artificial digestion, syntonin and peptone, the first and last terms of the process, alone are present.

As far as the products are concerned, artificial and natural digestion are similar, but essential differences occur in the time of appearance and disappearance of the various modifications of proteid. The artificial and natural digestion of fibrin are most alike. In artificial digestion, all three modifications are generally present from the beginning to the end of the digestion, but towards the end of natural digestion peptone is the almost exclusive product.

J. P. L.

Food of Larval Bees. By A. V. PLANTA (*Zeit. physiol. Chem.*, 12, 327—354).—The substance investigated was the juice or pap, the whitish sticky substance which the working bees store in the cells of the larvæ of the queens, drones, and workers. Leuckart (*Deutsche Bienenzeitung*, 1854, 1855) regarded it as the product of the true stomach of the working bees, which they vomit into the cells, in the same way that honey is vomited from the honey-stomach. Fischer and others regarded it as the product of the salivary glands of the bees. Schönfeld, in numerous papers, references to which are given, has more recently shown that Leuckart's original view is the correct one. He showed that the saliva can be easily obtained from the salivary glands of the head and thorax, and that it is very different from the food-juice deposited in the cells by the bees; and that, moreover, the juice is similar, both chemically and microscopically, to the contents of the bee's true stomach; he showed also from the consideration of certain anatomical and physiological peculiarities of the bee, such as the position of the mouth, the inability of the bee to spit, &c., that the view of this substance being saliva is quite untenable. Certain

observers have to this replied that a bee cannot vomit the contents of its true stomach, because of a valve which intervenes between it and the honey-stomach; but Schönfeld has shown that the structure, mistaken by these observers for a valve, does not function as one, but is in reality an internal mouth, over which the animal has voluntary control, and by means of which it is able to eat and drink the contents of the honey stomach when necessity or inclination arises. By light pressure on the stomach, and stretching out the animal's neck, the contents of the stomach can be easily pressed out.

The present investigations entirely confirm Schönfeld's view that this substance comes from the bee's stomach. The subject was investigated from the point of view of its chemical composition, and also care was taken to investigate, individually, the juice as occurring in the cells of the three varieties of bees, queens, drones, and workers.

Some preliminary microscopical examinations of this substance yielded the following results, which are quite in accord with the subsequent chemical analyses:—

1. The food of the queen-bee larvæ is the same during the whole of the larval period; it is free from pollen grains, which have been reduced to a thickish but homogeneous juice by the digestive action of the bee's stomach.

2. The food of the larval drones is also, during the first four days of the larval period, free from pollen, and appears to have been completely digested previously. After four days their food is rich in pollen grains, which have, however, undergone a certain amount of digestion. The food stuff of the larvæ is probably formed from bee-bread.

The following table gives the average percentages obtained from several analyses in most cases:—

	Food stuff of		
	Queen-bees.	Drones.	Working-bees.
Water	69·38	72·75	71·63
Total solids	30·62	27·25	28·37
In the solids—			
Nitrogenous material	45·14	43·79	51·21
Fat	13·55	8·32	6·84
Glucose	20·39	24·03	27·65
Ash	4·06	2·02	—

All kinds are thus rich in nitrogen; all were of a greyish-white colour; that of the queen-bee was the stickiest, that of the workers the most fluid. Peptone appeared to be absent; the greater part of the nitrogenous material present was proteid. The ethereal extract was in all cases acid, but formic acid was absent.

The sugar present was, in all cases, invert-sugar, whereas the sugar in pollen grains is invariably cane-sugar.

The table shows certain differences in the composition of the different kinds of larval food, more especially in the composition of the solids present. Its composition is, moreover, quite different from that of the bee's saliva, which, for instance, contains no sugar. The difference between the proportional amount of the different solids present in the different forms of larval food is a constant one, and no doubt this variation has in view the particular requirements of the larvæ in question. Certain small but constant differences were also observed in the chemical composition of the food of the larval drones during the first four days and at subsequent periods.

Not only is there a difference in the quality, but there is also one in the quantity of the food supplied. The juice from 100 queen-bee cells yielded 3.6028 grams of dry substance, that from 100 drones' cells 0.2612 gram, that from 100 workers' cells 0.0474 gram.

W. D. H.

Foddering of Horses, and the Circulation of Mineral Matter in the Horse. By E. WOLFF and others (*Bied. Centr.*, 1888, 241—252).—The question as to whether the albuminoids digested by the horse were really of higher value than a similar quantity of digested carbohydrates has not been satisfactorily answered; therefore a new set of experiments has been instituted with fodder rich and poor in nitrogen, and the work estimated by a dynamometer. Analytical tables are given showing the composition of the food and the manure produced, &c. The results obtained were: the digestible albumin has, above a certain minimum, no higher value as regards power of producing work than an equal quantity of starch-meal, or the starch equivalent of digestible cellulose and fat; field beans and maize are alike: to keep a horse of 500 kilos. weight in health and doing no work, 4200 grams weight daily of fodder is sufficient, provided that at least one-half consists of hay. As regards the circulation of the minerals in the horse, a large proportion of the lime (60—100 grams) is excreted as carbonate in the urine, causing that to be thick: of the magnesia one-third to two-fifths of the total quantity contained in the fodder appears in the urine, whereas the alkalis to the extent of 30 per cent. of the total is voided in the solids (sheep 5 per cent., oxen 10 to 12 per cent.). The phosphates also and the silicates are found altogether in the solids, whilst chlorine appears in the urine. As to the sulphates, they appear for the most part in the dung, and the more when the fodder is difficult of digestion and not too poor in nitrogen. The amount of urine voided is influenced by the percentage of digestible nitrogen and by the quantity of salts passing into the urine.

E. W. P.

Acetanilide and Acetotoluide in Relation to Animal Metabolism. By M. JAFFE and P. HILBERT (*Zeit. physiol. Chem.*, 12, 295—321).—Schmiedeberg (*Arch. f. exp. Pathol. u. Pharmacol.*, 8) has shown that aniline is probably oxidised in the body of the dog to form paramidophenol, which is passed in the urine in combination with sulphuric acid. A fresh examination into the fate of aniline com-

pounds in the body seemed to be necessary, as it is known that the amido-group often appears to modify the fate of complex aromatic molecules in the organism. The acetyl-derivative of aniline (antifebrin) is moreover of practical interest from its use in therapeutics. Experiments were made on dogs and rabbits, the urine of these animals being examined after the administration of these substances; the crystalline substances separated from the urine were purified by recrystallisation, their reactions carefully studied, and finally they were subjected to elementary analysis. The following are the results obtained:—

1. The change in acetanilide is different in herbaceous and carnivorous animals. (a.) In the rabbit, it is oxidised to form paramidophenol, with complete elimination of the acetyl-group. (b.) In dogs there is a small formation of paramidophenol, but the chief change consists in a simultaneous oxidation of the aniline residue to orthamidophenol, of the acetyl-group to carboxyl, and next a union occurs with the formation of phenylcarbamic acid, the anhydride of which, orthohydroxycarbanil, is excreted in the urine. The latter can be isolated in large quantities by heating extracts of that secretion with hydrochloric acid.

Both in rabbits and dogs, the metabolic products of acetanilide are excreted in combination with sulphuric acid.

2. The three isomeric acetotoluides differ in their chemical behaviour in the animal body. (a.) Paracetotoluide is changed completely into paracetamidobenzoic acid, oxidation being limited to the methyl-group. (b.) Orthacetotoluide undergoes in dogs a decomposition completely analogous to that suffered by acetanilide. Whilst the methyl-group remains intact, a phenol is formed which combines with the product of oxidation of the acetyl-group; the end (excreted) product being methyl hydroxycarbanil or hydroxycarbamidocresol, which may be regarded as the anhydride of hydroxycresylcarbamic acid; this product in the urine occurs in combination with sulphuric acid, and rotates the plane of polarised light to the left. (c.) Metacetotoluide is in dogs and rabbits oxidised to form metacetamidobenzoic acid, which is passed as a *lævorotatory* compound which was not further investigated.

3. Of the three isomeric acetotoluides, the ortho-compound is the only one which has poisonous properties.

4. The para- and ortho-compounds do not affect the body temperature; the meta-compound causes a lowering of the temperature. This shows that no inference can be drawn from the chemical constitution of these compounds, as to their effect on body temperature, for orthacetotoluide is completely analogous to antifebrin; it, therefore, might be fairly expected to have antipyretic properties; but, as just stated, experiment shows that it has not.

W. D. H.

Chylous Pericardial Fluid. By K. HASEBROEK (*Zeit. physiol. Chem.*, 12, 289—294).—A milky-looking fluid removed from the pericardium (*post-mortem*) of a patient at Strassburg (the clinical details of whose case are briefly given), was found microscopically to

contain the histological elements of chyle, but it did not yield any fibrin—even when a drop of blood was added to it.

Chemical analysis gave the following result (in parts per 1000) :—

Water	892·782
Solids	103·612
Proteids	73·789
Cholesterin.....	3·340
Lecithin	1·771
Fat	10·767
Alcohol-extractives	2·048
Water-extractives.....	2·555
Salts	9·336

On comparing these numbers with those which are the results of analyses of pericardial fluid by other observers, the following table is obtained :—

	1. Present case.	2. (Gorup-Besanez).	3. (Wachsmuth).	4. (Hoppe-Seyler).
Water.....	892·782	955·1	962·5	961·78
Solids	103·612	44·9	37·5	38·22
Fibrin	—	0·8	—	—
Albumin.....	73·789	24·7	22·8	24·63
Extractives	20·481	12·7	—	—
Salts	9·336	6·7	—	—

The solids in the present case are thus far in excess of those in ordinary pericardial fluids; the large amount of fat is equalled only in the chyle among the fluids of the body.

By further contrast of the numbers obtained in the present case with those in the very few existing analyses of the chyle, or of chylous effusions into the pleura and peritoneum, it is found that there is a close agreement not only in the percentage of fat, but also of total solid proteids, ethereal extract (cholesterin, lecithin, and fat). The conclusion is therefore drawn that the present case is not one of pericarditis, but of effusion from the lacteal vessels into the pericardium (chylopericardium).

W. D. H.

Toxic Action of Alcohols and Artificial Bouquets. By LABORDE and MAGNAN (*Chem. Centr.*, 1888, 18, from *J. Pharm.* [5], 16, 448—454).—The following are the chief results of experiments on dogs :—Ethyl alcohol from all sources was found to have the same physiological action. Furfuraldehyde, which occurs with pyridine and other impurities in commercial alcohols, has strong toxic properties. The distillate of Jamaica rum boiling at 83°, when injected subcutaneously, causes strong convulsions.

Salicaldehyde, which is added to “Vermuth,” “Bitter,” and “Essence de renie de Prés,” produces strong epileptic convulsions. Methyl salicylate, which is used as a substitute for oil of winter-

green in "Vermuth" and "Bitter," also produces convulsions, although not of an epileptic form.

Finally, benzonitrile and benzaldehyde, which are added in small quantities to "noyau," produce tetanus and even death.

J. P. L.

Physiological Action of Nickel Salts. By LABORDE and A. RICHE (*J. Pharm.* [5], 17, 1—11, 59—62, 97—105).—The action of nickel salts on the animal economy has been investigated with very contradictory results. Experiments were made on rabbits, &c., dogs and frogs by additions made to the food and by various methods of injection. Nickel sulphate, injected to the amount of 0.5 to 1.0 gram per kilo. body-weight, poisons a rabbit or dog. From 0.5 to 3.0 gram passed into the stomach produced vomiting and diarrhœa, but it is hardly possible to produce death this way. Nickel is considerably less active than copper, and its usual application in everyday life may be considered uninjurious.

J. T.

Chemistry of Vegetable Physiology and Agriculture.

Saccharomyces Ellipsoideus and its Use in the Preparation of Wine from Barley. By G. JACQUEMIN (*Compt. rend.*, **106**, 643—644).—Experiments have been made to determine whether *saccharomyces ellipsoideus* is a stable form or is merely an abnormal form of beer yeast developed under special conditions and liable to revert to the original form; but these experiments are not yet complete.

The action of elliptical yeast on barley wort produced a liquid with an alcoholic strength of 6° containing 60 grams of dry extract and 3 grams of ash per litre. It had the following percentage composition:—Alcohol, 4·80; reducing sugar, 1·00; dextrin, 3·00; albuminoids, &c., 1·28; glycerol, 0·20; succinic acid, 0·04; acetic acid, 0·02; potassium hydrogen tartrate, 0·25; ash, 0·23; water, 89·18. The liquid has an agreeable flavour, and contains a greater proportion of albuminoids and phosphates than wine from grapes. It differs from the latter in giving an abundant precipitate with tannin. The barley may be partially replaced by crushed wheat. Barley and wheat worts are cheaper than malt worts, and give products of equal quality. To obtain a liquid with an alcoholic strength of 8° or 10°, it is necessary to mix the wort with sugar or to use a greater proportion of grain.

In these experiments it was found that the elliptical wine yeast remained stable for 18 months, and it would therefore seem to be quite distinct from beer yeast.

When the wine obtained in this way from barley is distilled, it yields brandy of good flavour, whilst the brandy from wine produced by beer yeast has a bad flavour.

C. H. B

Direct Assimilation of Vegetable Remains by Chlorophyll-containing Plants. By L. KOCH (*Chem. Centr.*, 1888, 13—14, from *Ber. deut. bot. Ges.*, 5, 350—364).—The present observations relate to the saprophytic mode of life of *Melampyrum pratense*. The author describes the development of the root organs upon which the plant depends for its close attachment to the nutritive material. Compared with the mother root, they form moderately large balls, the thin-walled polygonal cells of which are filled with colourless, protoplasmic bodies of a curved rod-like form which appear to correspond with the bacterioides of the root-swellings of the Leguminosæ. Formed starch is not present. These cells play the part of reserve stores, and they break down when their contents are used up. All the author's observations lead to the conclusion that *Melampyrum* assimilates dead and not living parts of plants, consequently it is a saprophyte and not a parasite.

As the plant contains large quantities of chlorophyll it can readily supply its wants so far as non-nitrogenous food is concerned, and the nitrogenous food is probably supplied by the material stored in the polygonal cells—a conclusion which receives some support from the absence of formed starch in these cells.

J. P. L.

Behaviour of Formose in contact with Vegetable Cells Deprived of Starch. By C. WEHMER (*Ann. Agronom.*, 14, 40—41, from *Bot. Zeit.*, 45, 713).—This research bears on the suggestion that the first product of the assimilation of carbonic anhydride in the plant cell is the formose of O. Loew, a substance formed by the condensation of formic aldehyde, and having a sweet taste, the power of reducing Fehling's solution, and some colour reactions in common with the sugars. It is, however, not fermentable; is without action on polarised light; does not yield the same acid by treatment with weak acids, nor the same substance by combination with phenylhydrazine as the true carbohydrates of the dextrose class. From this it seems doubtful whether it is a true carbohydrate, and the author's experiments strengthen this doubt, for they show that whereas leaves deprived of starch by being placed for some time in darkness have the power of forming starch when placed in solutions of dextrose and cane-sugar, they did not form any starch when placed for even 14 days in a 5 per cent. solution of formose. In this respect formose resembles erythrol.

J. M. H. M.

Behaviour of Formose in Contact with Vegetable Cells Deprived of Starch. By C. WEHMER (*Bied. Centr.*, 1888, 268).—The leaves of *Fraxinus ornus*, *Rubia tinctorum*, *Syringa vulgaris*, and *Cacalia suaveolens*, formed no starch when in contact with a 5 to 10 per cent. solution of formose (from formaldehyde), whilst starch was formed from dextrose and saccharose, confirming the results previously given (preceding Abstract).

E. W. P.

Absorption of Salts by Plants. By BERTHELOT and G. ANDRÉ (*Compt. rend.*, 106, 801—805 and 902—906).—*Amarantus caudatus*, *A. pyramidalis*, and *Portulacca oleracea* were grown in large pots con-

taining about 50 kilos. of earth to which a large proportion of a soluble potassium salt had been added, care being taken that the quantity of water present was sufficient to keep the whole of the salt in solution.

Potassium sulphate was added in the proportion of 395·4 grams to 45·5 kilos. of soil. The observations afford further evidence of the tendency of potassium to accumulate in the leaves, but the quantity of potassium salts present is always below that required to form a saturated solution. If this limit is reached, the plant dies. The proportion of potassium in the flowers is about one-half, the proportion of potassium sulphate about one-tenth, of that in the leaves. On August 2nd, one-sixth of the total potassium was in the root, one-fifth in the stalks, and one-third in the flowers; on September 20th, one-fourth was in the root, one-fifth in the stalk, a tenth in the flowers, and half in the leaves. With the exception of the flowers, the juices of the plant become richer in sulphates as they travel from the roots to the leaves.

The general results show that endosmotic or other changes between the soil and the juices of the plants employed obey the usual law, the solution which is in contact with the roots remaining richer than the solution which passes through the roots into the plant. This is the more important, since in *Amarantus* the proportion of nitrates is much higher than in the soil, and hence these salts would tend to pass from the plant to the soil, and not *vice versâ*. The low proportion of sulphates in the stalks of *Amarantus* contrasts strongly with the tendency of the nitrates to accumulate in this part of the plant.

Potassium acetate was examined in a similar manner—327·7 grams of the salt being added to 45·5 kilos. of soil. The earth became alkaline owing to the decomposition of part of the acetate, and brown humous substances were formed which at first interfered with the growth of the plants. The following results were obtained on September 21st:—

	Root.	Stalk.	Leaves.	Flowers.
Moist plant	8·9	118·3	38·1	20·8
K ₂ O, absolute	0·119	1·529	0·636	0·231
K ₂ O, relative.....	5·2	5·9	8·0	5·5

The total quantity of potassium is not greater than in the same plants grown in ordinary soils; its accumulation in the stalks is in agreement with the authors' previous observations (*Ann. Chim. Phys.* [6], 5, 547). The proportions in different parts of the plants are within the limits of variation in *Amarantus* under ordinary conditions, and hence it follows that the presence of a large quantity of potassium in the soil in a readily assimilable form has no marked influence on the absorption of this element by the plant.

Potassium nitrate was added in the proportion of 361·5 grams per 45·5 kilos. of soil. As in the other experiments, the total quantity of potassium in the plant and its general distribution were not affected by the presence of the large quantity of a potassium salt in the soil. On September 21st, a plant with a few flowers gave the following results:—

	Root.	Stalk.	Leaves.	Flowers.
Moist plant	55·4	383·8	124·5	13·3
K ₂ O, total.....	0·897	6·444	2·490	0·187
K ₂ O, relative	5·1	7·7	6·8	4·6

These and other observations show that when the plant flowers the relative proportion of nitrates diminishes. A comparison of these results with those obtained with *Amarantus* growing in fields (*Ann. Chim. Phys.* [6], 8, 56) shows that the formation of potassium nitrate depends chiefly on the period of growth of the plant and not on the proportion of this salt existing in the soil. It attains the same order of magnitude in natural soils in which the ratio of nitrate to water is small as it does in artificial soils in which this ratio is very high, and hence is not dependent on the degree of saturation of the water in the soil. In the experiments described, the concentration of the nitrate solution in the soil was much greater than the possible concentration of the solution in the plant, whilst in the former experiments the solution in the plant itself was much stronger than the solution in the soil. It obviously cannot be assumed that the nitrates are absorbed from the soil, but they must be formed in the plant itself.

C. H. B.

Production of Oxygen by Green Cells. By N. PRINGSHEIM (*Ann. Agronom.*, 14, 41—43, from *Ber. deut. bot. Ges.*, 5, 294—307).—The author, from his microscopical researches on the assimilation of carbonic anhydride by plants, concludes that the disengagement of oxygen, and decomposition of carbonic anhydride, hitherto considered as two manifestations of one and the same vital act, are really two separate phenomena, not simultaneous, and taking place in different spots, the latter occurring first in the interior, and the former afterwards on the surface, of the living cell. He supposes a third substance formed, or set at liberty, as the result of the decomposition of the carbonic anhydride, and having the power of giving up oxygen when it arrives at the surface of the cell.

J. M. H. M.

Oxidation in the Plant. By J. REINKE (*Ann. Agronom.*, 14, 43—45, from *Ber. deut. bot. Ges.*, 5, 216—220).—The author considers that respiration is a purely chemical and not a vital phenomenon, and cites in support the fact that respiration is not arrested by the death of the cell, but that leaves killed by a prolonged exposure to ether vapour continue to emit carbonic anhydride a long time after death. Another explanation of this fact is given in the following Abstract.

J. M. H. M.

Continuation of Respiration in Dead Vegetable Cells. By W. JOHANNSEN (*Ann. Agronom.*, 14, 134, from *Bot. Zeit.*, 1887, 162).—The evolution of carbonic anhydride due to respiration diminishes gradually in a dying plant, and ceases at the point of death. Oxidation recommences in the dead cells after a little time, but only as the ordinary oxidation of dead matter, due either to bacteria or to purely chemical agencies. The two phenomena may be distinguished thus: if a living cell is deprived of free oxygen, carbonic anhydride continues

to be evolved by intramolecular respiration. If a dead cell be placed in the same conditions this does not take place. J. M. H. M.

Assimilation and Expiration of Plants. By U. KREUSLER (*Bied. Centr.*, 1888, 265—267).—This set of experiments was instituted to ascertain the influence of lower temperatures on the assimilation of plants. The plants observed were bramble, bean, castor-oil, and cherry laurel, the conditions of experiment and the methods employed were the same as on former occasions (this vol., p. 186), but the temperatures were lower. At 0°, the exhalation of carbonic anhydride was 17 to 20 per cent. of that which occurs at 20° in the case of the laurel and castor-oil plant; in the case of the bramble, the exhalation was only one-half of that at 10°. Assimilation at 0° is for the laurel only 8 per cent. of the possible maximum. E. W. P.

Absorption of Nitrogen by Plants. By HELRIEGEL and WILLFARTH (*Bied. Centr.*, 1888, 228—230).—Experiments were made in boxes in which were sown oats, peas, buckwheat, &c. It was found that those of the order *Papilionaceæ* were able to grow and flourish long after all the nitrogen present in the soil had been absorbed by them, whereas oats, &c., only grew as long as there was any of the nitrogen left that had been originally contained in the seed, &c. E. W. P.

Influence of Camphor on the Germination of Seeds. By A. BURGERSTEIN (*Landw. Versuchs-Stat.*, 1888, 1—18).—Commencing with a *résumé* of the work done by Vogel, Wilhelm, and Nobbe, and having pointed out the disagreement which exists between the results obtained, the author passes on to an account of his own experiments in which seeds of different ages and varieties of plants were grown and watered with a solution of camphor, time was also introduced as a factor in these experiments, the results being that camphor-water has an influence on germination, the influence depending on the time. A preliminary soaking in camphor-water has a detrimental effect on all seeds of whatever kind or quality they be, and this influence consists in a retardation of the process of germination, in a reduction in the percentage of germination, and in a reduction in the length of the sprouts during the earlier periods; moreover, absorption of camphor-water for only 12 hours weakens the germinative power. When the period of soaking was only 1 to 12 hours, then out of 27 seeds, 8 were accelerated in their growth, and 9 retarded in germination, whilst the remaining 10 were apparently alike as regards camphor compared with distilled water. No apparent change from normal colour was noticeable—the author cannot agree that camphor revivifies the germinative power of seeds, as Vogel states. E. W. P.

Distribution of the Ash in Trees. By WEBER (*Ann. Agronom.*, 14, 143—144, from *Bot. Centr.*, 32, 314).—A beech-tree, 150 years old, having been felled, a slice was cut off at every 5 metres of height, and from each slice were separated the layers corresponding to 30 annual ligneous rings. Analyses of the samples thus taken, showed that in a zone of the same age the quantity of ash increases regularly

from the base of the trunk to the summit. At the lower part of the trunk the ash increases from the periphery to the centre up to a certain limit, beyond which it decreases towards the axis. In the slices cut off higher up the trunk, the increase of ash from periphery to centre goes on right through the section. The bark is much richer in ash than the wood.

As regards the composition of the ash, the potash increases from the exterior to the interior (from 23 to 43 per cent.) whilst the phosphoric acid, sulphuric acid, and magnesia diminish in the same direction, the magnesia falling from 29 to 11 per cent. and the phosphoric acid from 8 to 2 per cent. The variation in the lime is slight and irregular. In the bark, lime predominates greatly, amounting to 82 per cent., whilst the potash, magnesia, and phosphoric acid amount only to 4 to 1 per cent.

J. M. H. M.

Phosphorus and Phosphoric Acid in Plants. By BERTHELOT and G. ANDRÉ (*Compt. rend.*, 106, 711—716).—Experiments with *Amarantus caudatus* and *A. pyramidalis*, protected from rain but freely exposed to the air, show that the plant absorbs both phosphorus and potassium from the soil in the early stages of its growth, though the amount of both, and especially of phosphorus, increases less rapidly than the weight of the plant. When inflorescence begins, the absorption of phosphorus practically ceases, but the absorption of potassium continues so long as the plant grows, and the increase in the quantity of this element during flowering is very considerable. The increase in the quantity of nitrogen is almost proportional to the increase in the weight of the plant up to the beginning of inflorescence, although somewhat smaller in the early stages of growth. When the plant flowers, the total quantity of nitrogen increases but little, and therefore the proportion of this element decreases.

In a soil containing about 8 grams of potassium acetate per kilo., the plants grew with some difficulty, but those which survived became much larger. They contained nearly twice as much potassium as under normal conditions, but the increase in the amount of phosphorus followed the ordinary law. The following example is typical of all the experiments.

	Weight of plant.	Phosphorus.	
		Absolute.	Relative.
May 31st.	1·693 grams.	0·0032	1·7
July 5th.	12·6 "	0·0265	0·73
August 2nd.	14·68 "	0·0281	0·67
September 30th.	22·58 "	0·0262	0·33

	Potassium oxide.		Nitrogen.	
	Absolute.	Relative.	Absolute.	Relative.
May 31st	0·0057	3·2	0·0041	2·3
July 5th	0·071	2·0	—	—
August 2nd.....	0·166	4·0	0·091	2·2
September 30th	0·251	3·0	0·103	1·2

On August 2nd, the plant had begun to flower, and on September 30th it had begun to die.

From these results it follows that manures containing phosphorus and nitrogen are of no value after the plant has begun to flower, but manures containing potassium may be useful throughout the whole period of growth.

C. H. B.

Acidity of Cell Sap. By LANGE (*Ann. Agronom.*, 14, 134—135, from *Bot. Centr.*, 32, 236).—The author finds that acidification of the cell-sap during the night, and the disappearance of acid during the day, are changes not special to one or two groups of plants, but common to plants of all classes. The diurnal de-acidification is more energetic in the red half of the spectrum than in the blue. In this the author's results agree with those of Kraus and Warburg, and are opposed to those of de Vries.

J. M. H. M.

Saccharine Matter in Peach-gum. By R. W. BAUER (*Landw. Versuchs-Stat.*, 1888, 33—34).—Peach-gum was boiled with 5 per cent. sulphuric acid for four hours, then neutralised with chalk, the filtrate after evaporation to a syrup extracted with alcohol, and the filtrate evaporated over sulphuric acid. The syrup remained unaltered some months, but after the introduction of a small quantity of pure dextrose, galactose, and arabinose, a mass of crystals was formed. After purification, these crystals seemed to be identical with galactose from agar-agar.

E. W. P.

Injury to Plants by Kiln Smoke. By E. W. PREVOST (*Landw. Versuchs-Stat.*, 1888, 25—28).—The results obtained corroborate the observations of Schroeder (*Bied. Centr.*, 1884, 535) and Reuss, as regards the damage effected by smoke from furnaces; in this special case, the fumes came from brick-works, and the leaves of the various plants (rhubarb, pear, pine, larch trees, &c.), all showed brown spots on them, and in the case of the pines and larches the ends of the needles were affected; analyses show an increase of sulphuric acid in the leaf. The author is of opinion that leaves may be in an unhealthy state without any visible signs, these signs only appearing at a later date; he draws this conclusion from the fact that some samples which were collected and appeared to be healthy, showed minute spots on them after having been removed from the deleterious atmosphere for 12 hours.

E. W. P.

Percentage of Sulphuric Acid in Plants Damaged by Sulphurous Anhydride. By E. MACH (*Landw. Versuchs-Stat.*, 1888, 52—53).—Hay made from grass which had been damaged by fumes from a cellulose factory in the Tyrol was submitted to analysis; the results showed that the percentage of water was much reduced, from 13·65 to 7·55 per cent., the pure ash was reduced from 9·77 to 8·36, whilst the sulphuric acid was raised in the dry matter from 0·54 to 0·818 and 0·96, and in the pure ash from 6·35 to 8·64 and 11·59.
E. W. P.

Titanic Oxide in Soils. By G. F. McCALB (*Amer. Chem. J.*, 10, 36—37).—Using Weller's hydrogen peroxide colorimetric test (*Abstr.*, 1883, 381), a number of samples of soil from Virginia, U.S., have been examined, and all found to contain titanic oxide in quantities varying from 0·3 to 2·8, and even 5·4 per cent.
H. B.

Sources of the Nitrogen of Vegetation. By J. B. LAWES and J. H. GILBERT (*Proc. Roy. Soc.*, 43, 108—116).—Land which had been exhausted of nitrogen by successive crops of beans, gave a very large crop when sown with barley and clover. Numerous experiments were made to determine the source of the nitrogen. As the surface soil was richer in nitrogen after the crop had been grown, the nitrogen could not have been derived from that source. The clay subsoil was found to be susceptible to nitrification, especially in the presence of Leguminosæ, but the necessary secretion was a difficulty. In order to see if the acidity of the sap could account for the nitrogen obtained, soils were treated with organic acids. The amount of nitrogen obtained in this way was small, and less after long than after short contact. The nitrogen so taken up seems to exist in the soil in the form of amides, and the question arises whether the plant takes up the amide as such or converts it into ammonia and nitric acid. To test this, urea, uric acid, hippuric acid, quinine, ammonium phosphate, glycocine, creatine, and tyrosine were used in the water-culture method and in soil. Nitrogen was undoubtedly taken up, but in the soil experiments the organic compound appeared to have been decomposed; urea appears to be taken up as such. The evidence as to whether nitrogen is taken up from the air is very conflicting. The absorption, if any, has been attributed to electrical action, or to the agency of micro-organisms. In any case, the amount taken up would not suffice for the compensation usually supposed to take place.
H. K. T.

Conversion of Nitrates in Soils into Nitrogenous Organic Compounds. By BERTHELOT (*Compt. rend.*, 106, 638—641).—43·3 kilos. of moist earth, containing 72·3 grams or 1·669 grams per kilo. of organic nitrogen, was mixed with 361·5 grams of potassium nitrate, and a quantity of water sufficient to produce a 4 per cent. solution of the nitrate. The earth was then exposed to the air for six months, care being taken to protect it from rain. At the end of this time, the amount of organic nitrogen had increased by 16·4 grams or 0·3777 gram per kilo., a quantity equal to about one-fourth of the

original organic nitrogen, and about one-third of the nitrogen in the potassium nitrate.

A similar quantity of earth with the same quantity of alkaline nitrate was planted with 11 roots of *Amarantus pyramidalis*, weighing 1.899 grams. After growth, the total weight of the dried plants was 197.2 grams, and they contained 5.83 grams of nitrogen. The quantity of organic nitrogen in the soil was practically the same as at the end of the first experiment, and was equal to about one-third of the nitrogen in the nitrate. The quantity of nitrogen and of nitrates in the plant was much below that found in former experiments, notwithstanding the large proportion of nitrate in the soil. It follows that the formation of nitrates in *Amarantus* is a complex process.

The assimilation by plants of the nitrogen existing in soils as nitrates is preceded or accompanied by a conversion of the nitrogen of the nitrates into nitrogenous organic compounds in the soil, either by the action of microbes or by pure chemical processes.

In all soils the formation of nitrates by the action of aerobic microbes is opposed by the action of the anaerobic microbes, which produce fermentative and putrefactive changes and thus tend to reduce the nitrogen to nitrogenous compounds, or even to cause its liberation in the free state. The antagonism between these two classes of organisms explains the fact that nitrification reaches a limit before the whole of the nitrogen present is converted into nitrates. C. H. B.

Absorption of Nitrogen by Soils and Plants. By A. GAUTIER and R. DROUIN (*Compt. rend.*, **106**, 754—757, 863—866, and 944—947).—An artificial soil (A) was prepared by mixing 60 parts of Fontainebleau sand, washed with strong acids and then with water, and containing 0.5 per cent. of gelatinous silica, with 30 parts of pure precipitated calcium carbonate, 10 parts of pure washed kaolin, and 3 parts of neutral potassium phosphate. A second soil (B) was prepared by mixing A with 5 per cent. of ferric oxide; a third (C) by mixing 1100.25 grams of A with 22.5 grams powdered wood charcoal, washed with acids, and 2.25 grams of ulmic acid from sugar and hydrochloric acid; and a fourth (D) by mixing 1062.7 grams of A with 37.5 grams of ferric oxide, 22.5 grams of charcoal, and 2.25 grams of ulmic acid.

Quantities of the soils, with or without vegetation, were exposed to the air in pots in such a manner that they were completely permeable by the air, but were protected from rain. The total nitrogen was determined by a modification of Dumas' process, and the ammonia and nitrates by Schloesing's method. The quantity of soil used in each experiment was about 1200 grams.

A first series of observations was made with the four soils in which no plants were growing, the exposure to air extending from August 14th to October 31st, 1887, the soil being watered from time to time. With A, the total nitrogen diminished from 0.1181 to 0.1137 in one case and 0.1054 in another, the losses being respectively 0.0044 and 0.0127; with B, it diminished from 0.1252 to 0.0987 in one case and 0.1106 in another, the losses being 0.0294 and 0.0175 respectively.

When the soil contained organic matter, however, the results were different. With C, the nitrogen increased from 0·2344 to 0·3349, or a gain of 0·1005; with D, it increased from 0·2437 to 0·2592 in one case and 0·4451 in the other, the gain being 0·0155 and 0·2014 respectively. The small increase in the first case is due to the fact that the earth had settled in the pot, and was much less permeable to the air.

The same soils were sown with broad beans, which assimilate considerable quantities of nitrogen and are regarded by agriculturists as constituting a crop which enriches the soil in this element. The following results were obtained, the beans being sown on August 14th, and the plants cut down at the end of October:—

	Total nitrogen.		Increase.	Nitrogen in the soil.	
	Before.	After.		Before.	After.
Soil A	0·3566	0·5372	0·1806	0·1151	0·1782
Soil B	0·3666	0·5341	0·1675	0·1252	0·1558
Soil C	0·4724	0·6797	0·2073	0·1126	0·3238
Soil D	0·4806	0·7288	0·2482	0·1224	0·3145

These results show that soil free from organic matter loses part of its nitrogen when exposed to the air, but if it contains organic matter it is able to absorb nitrogen from the air independently of vegetation. When, however, the soil is supporting vegetation, a still greater quantity of nitrogen is absorbed by those which contained organic matter, and a considerable quantity is absorbed by soils which previously contained no organic matter, and hence of themselves absorbed no nitrogen.

C. H. B.

Relation between Atmospheric Nitrogen and Vegetable Soils. By T. SCHLOESING (*Compt. rend.*, 106, 805—809, and 898—902).—It has already been shown that nitrogen, like oxygen, cannot undergo any physical condensation in the pores of ordinary vegetable soil. If nitrogen is absorbed from the atmosphere, it must be fixed chemically or otherwise by the organic matter, since none of the inorganic constituents of the soil absorb nitrogen. Boussingault found that when air and soil were allowed to remain in contact for 11 years in hermetically sealed flasks, there was no increase in the quantity of nitrogen in the soil, but some of the nitrogenous organic matter was converted into nitrates at the expense of the oxygen of the air. In consequence of the direct contradiction between these results and those recently obtained by Berthelot and André, the author has repeated Boussingault's experiments with certain modifications.

The soil was enclosed in flasks with long necks, which were rendered vacuous, and pure air of known composition was allowed to enter. The necks were then bent over, and the open ends placed under mercury. The neck of each flask contained a quantity of

calcium oxide, which absorbed the carbonic anhydride produced by the oxidation of the organic matter in the soil, and the absorption of oxygen was indicated by the rise of the mercury in the neck. Pure oxygen was introduced from time to time in order to maintain an excess of this gas in the atmosphere in the flask. After a sufficient length of time, the air remaining in the flask was analysed. By operating in this manner the accurate methods of eudiometry are substituted for the much less accurate plan of determining the amount of nitrogen in the soil. Complete details of the experiments are given in the second paper. Six soils of different character were employed. In each case, there was a large absorption of oxygen, with evolution of carbonic anhydride, the combustion of the organic matter in the soil proceeding to an extent varying with the nature of the soil. During this combustion, nitrates are formed, and the ammonia in the soil disappears. The variations in the volume of the nitrogen in the globes are not greater than the errors of experiment; the greatest variation actually observed corresponds with the absorption of 16 kilos. of nitrogen in 14 months by 4000 tonnes of soil, arranged in a layer 0.3 metre deep. C. H. B.

Mealy and Steely Barley. By W. JOHANNSEN (*Landw. Versuchs-Stat.*, 1888, 19—23).—After several samples of barley had been moistened with an equal quantity of water, and then dried, it was found that the mealiness of the grain was dependent on the percentage of nitrogen, thus grains containing less than 1.41 per cent. N showed a degree of mealiness denoted by 95, whereas those containing 2.00 per cent. were classed as 30. Experiments further showed that if steely barley is slightly moistened and then dried, it will yield as good a malt as if it had been more mealy. E. W. P.

Sugars and Starch in Fodders and their Determination. By E. F. LADD (*Amer. Chem. J.*, 10, 49—53).—With wheat and its products, freshly prepared diastase gives an amount of starch (as determined by Fehling's solution) comparing favourably with that obtained by inversion with acid; but diastase hardly acts on the starch contents of hay and similar products. As regards the inversion by acids, it was found that with starch rather higher results were obtained by the use of sulphuric acid, but with hays and fodders more uniform and slightly higher figures were obtained by the use of hydrochloric acid. The amount of hydrochloric acid necessary is 3 to 5 c.c. for 5 grams fodder, or 3 grams starch and 150 c.c. of water; the action is complete in 11 hours. A number of analyses are given, showing the percentages of saccharose, glucose, starch, nitrogen-free extract and starch in various corns and fodders; the influence of the time of cutting and the action of various fertilisers are also briefly referred to. H. B.

Farmyard Manure. By P. P. DEHÉRAIN (*Ann. Agronom.*, 14, 97—133).—As to the result of a survey of his own work and that of others, the author concludes that litter impregnated with the solid

and liquid excreta of animals and placed upon a floor, undergoes the following changes:—

1. Solution of the vasculose and of a large proportion of the nitrogenous matter by the alkaline carbonates, the dissolved material constituting the dark brown colouring substance of the liquid drainings of the dung-heap.

2. Destruction of a great part of the cellulose of the litter by fermentation, with disengagement of methane and carbonic anhydride: the insoluble residue which persists after the loss of part of the nitrogenous matter, vasculose, and cellulose, consists of vasculose unattacked at the ordinary temperature; it is this residue, rich in vasculose partially altered by loss of water, which is often called "black butter."

3. Transformation of ammonia (arising from the fermentation of urea) into nitrogenous organic compounds, in great part soluble in alkaline liquids; this change is produced solely by living ferments.

4. During this fermentation, part of the nitrogen escapes in the free state, for when the manure is sufficiently moist very little loss of ammonia occurs.

J. M. H. M.

Waste Products as Manure (Bone-meal). By A. PETERMANN (*Bied. Centr.*, 1888, 230—239).—These experiments, in which bone- and blood-meal mixed with potassium chloride, Chili saltpetre, or bone-ash were used, have been conducted for three years on clay and sandy soils in the neighbourhood of Gembloux. It was found that the simple addition of phosphates (bone-ash) to this sandy clay was of little or no value, but that when an addition of nitrogen was also made, as in bone-meal, then there appeared an increase in the yield of the crop; the results obtained from this mixture were far surpassed, however, by those obtained by the use of blood-meal, or phosphates with saltpetre and potash. The results obtained on the sandy soil were in all cases inferior to those on the heavy land: the best results were produced by the employment of blood-meal, bone-ash, and potash. Reviewing all his experiments made since 1880, the author comes to the conclusion that the various nitrogenous manures stand in the following order as regards manurial value: Saltpetre, dried blood, dissolved wool, bone-meal, raw wool, and leather-meal. E. W. P.

Addition of Wood-ashes to Superphosphates. By V. T. MAGERSTEIN (*Bied. Centr.*, 1888, 225—226).—An admixture of wood-ashes with superphosphates has long been known as advantageous, but the addition must not exceed 25 per cent., otherwise the lime which is thus added will cause a loss by reason of the formation of reduced phosphate. E. W. P.

Manuring Experiments with Various Phosphates. By E. GATELLIER (*Bied. Centr.*, 1888, 227—228).—As superphosphates are supposed to be reduced by the bases in the soil, and thus to become equal to insoluble phosphates, experiments were instituted to test the value of varieties of phosphates on clay soils in France; in all cases bone superphosphate (16 per cent. sol.) surpassed basic slag, ordinary superphosphate, &c. E. W. P.

Analytical Chemistry.

Thompson's Calorimeter. By SCHEURER-KESTNER (*Compt. rend.*, **106**, 941—944).—The proportion of oxidising mixture necessary for complete combustion varies with the nature of the coal and the proportion of ash which it contains. The author employed from 10.5 to 12.5 times the weight of the coal; with only 10 parts of oxidising mixture, the combustion is usually incomplete. The correction of 10 per cent. usually added to the results is much too low. Experiments with ignited wood charcoal showed that for the author's apparatus 15 per cent. was the true correction. This was used for samples of coal, the heat of combustion of which had previously been determined by Favre and Silbermann's method; the maximum difference was 1.25 per cent. The heat of combustion of 20 coals was determined by Thompson's calorimeter, and afterwards by Favre and Silbermann's apparatus. The variations were sometimes on the one side, sometimes on the other, the maximum difference being 3.5 per cent. In 11 cases, the difference was less than 2 per cent.

Although Thompson's calorimeter gives results of practical value, when an error of 2 or 3 per cent. is negligible, it is only worthy of limited confidence. Berthelot's calorimetric bomb would be much better. The main sources of error, as Stohmann has pointed out, are the heat of decomposition of the oxidising mixture and the heat of dissolution of the salts after combustion, since the proportion of each salt varies with each coal. Some finely powdered samples of coal which had been exposed to diffused light for 20 years in bottles not very tightly closed, were found to be completely unaltered. C. H. B.

Improved Form of Gas Apparatus. By J. T. WILLARD (*Amer. Chem. J.*, **10**, 53—56).—The apparatus is essentially a combination of Elliott's (Abstr., 1887, 1137) and Frankland's. H. B.

Preservation of Solutions of Hydrogen Sulphide. By D. LINDO (*Chem. News*, **57**, 173—175).—The hydrogen sulphide is readily estimated in fresh solutions of this gas containing glycerol, camphor, boric acid, or thymol, by precipitation with silver nitrate and ammonia, filtering on a Gooch filter, drying, and weighing. In old solutions containing glycerol, silver nitrate does not answer, therefore the author employs sodium arsenite and hydrochloric acid for the precipitation. This precipitate is, however, troublesome to wash, and is best kept as small as possible, or if precipitated along with prepared asbestos, by adding some of the latter to the solution before precipitation, it may be washed with comparative ease.

From numerous experiments made in Jamaica in closed and open bottles at an average temperature of 26°, the author concludes that there is no advantage derived from the use of glycerol for the preservation of solutions of hydrogen sulphide.

Moreover, the other substances mentioned above do not prevent

loss in strength by escape of gas, but camphor and thymol appear to retard oxidation.

D. A. L.

Rapid Determination of Hydrogen Peroxide. By CONTAMINE (*Dingl. polyt. J.*, **267**, 238).—A few c.c. of the solution under examination is introduced into a glass tube divided into tenths of a c.c., and sealed at one end. Having previously neutralised the solution with ammonia, the volume is read off. A few crystals of potassium permanganate enclosed in tissue paper are then added, after which the aperture is closed with the finger and the tube shaken vigorously. It is then opened under water and the volume read off. The difference between the two readings gives the quantity of oxygen contained in the hydrogen peroxide solution. The method is sufficiently accurate to be used in works for determining the quantity of hydrogen peroxide in bleaching solutions.

D. B.

Supposed Occurrence of Hydrogen Peroxide in Animal and Vegetable Juices. By T. BOKORNY (*Ber.*, **21**, 1100—1102).—Wurster's tetramethylparaphenylamine reaction (*Abstr.*, 1887, 295) is useless as a test for hydrogen peroxide in animal and vegetable juices, since the paper is turned blue by very many compounds, such as nitrites, moist silver oxide, quinone, aldehyde, acetone, &c. For this reason, the reaction is no proof of the presence of hydrogen peroxide. Experiments have shown that living protoplasm does not give the ordinary reactions for hydrogen peroxide.

F. S. K.

Gravimetric Estimation of Chlorine. By F. STOLBA (*Chem. Centr.*, 1887, 1240, from *Listy. Chem.*, **11**, 224—225).—In the case of small quantities of chlorine (up to 80 milligrams) in water, &c., the author precipitates the chlorine as silver chloride, collects the precipitate on a large Schleicher-Schuell filter-paper, dries, and so folds the paper that the precipitate is enveloped at the point in many folds of paper, the paper is very slowly carbonised in a platinum capsule, the carbon burnt off at a low temperature, and the remaining spongy silver weighed and tested as to its complete solubility in nitric acid.

J. P. L.

Volumetric Determination of Sulphuric Acid. By A. GAWALOWSKI (*Zeit. anal. Chem.*, **27**, 152—159).—The principle of the method is identical with Wilsing's (*Abstr.*, 1887, 181). The titration with sodium carbonate is, however, made in the cold after the addition of a few drops of alcohol. Boiling is said to favour the end reaction, but not to be absolutely necessary. The mixture of the sulphate with the barium chloride should be allowed to remain for $\frac{1}{4}$ or $\frac{1}{2}$ hour before titrating the excess, and a similar interval should be allowed before finally judging of the completion of the titration with sodium carbonate. Seminormal solutions are recommended. The test analyses show errors of 1 per cent. in both directions.

M. J. S.

Volumetric Estimation of Sulphuric and Phosphoric Acids. By J. T. WHITE (*Chem. News*, **57**, 165—166; 187).—Sulphuric acid in combination with fixed alkalis may be estimated by titration with

silver nitrate and potassium chromate in the following manner:—Precipitate the solution with excess of barium chloride, and remove the barium remaining in solution with ammonium carbonate, then evaporate, ignite, and titrate the resulting alkaline chlorides in the ordinary fashion. If phosphoric acid is also present, precipitate it beforehand with magnesium chloride and ammonia. One portion of this filtrate is then evaporated with ammonium chloride, and the ignited residue titrated; whilst another portion is treated as above for sulphuric acid; the difference between the two results is the chlorine due to the decomposed sulphates. To estimate phosphoric acid in alkaline phosphates, decompose chlorides if present by evaporation with sulphuric acid, neutralise with soda, precipitate with excess of silver nitrate solution, neutralise with calcium carbonate, and titrate the excess of silver nitrate in the usual way. The presence of sulphuric acid does not interfere, as the solution is kept sufficiently dilute to dissolve silver sulphate.

D. A. L.

Estimation of Total Nitrogen. By HOUSSEAU (*Chem. Centr.*, 1888, 82—83, from *Pharm. Centr.*, 28, 627—628).—The process depends on the fact that all nitrogenous substances yield the whole of their nitrogen in the form of ammonia when heated with sodium acetate, sodium thiosulphate, and soda-lime.

The mixture of sodium acetate and thiosulphate is prepared by melting equal parts by weight of both salts in their water of crystallisation on a water-bath and powdering the cooled residue.

The combustion is performed in precisely the same manner as in the Will-Varrentrap process, about 2 grams of the mixture with 2 grams of soda-lime at the end of the tube supply the necessary indifferent gases to drive off the last of the ammonia.

J. P. L.

Sources of Loss in the Determination of Nitrogen by Soda-lime. By W. O. ATWATER and E. M. BALL (*Amer. Chem. J.*, 10, 113—119).—The following directions are given as being necessary. The anterior portion of the tube must be tightly packed with coarse soda-lime, not with fine, and there must be no appreciable open channel along the upper portion of the tube, otherwise, losses amounting to 6.4 per cent. of the nitrogen may occur. The anterior layer is the first part of the tube heated. The time of combustion should not be too protracted, $2\frac{1}{2}$ hours for instance, as this may introduce an error of 2.8 per cent., and if the tube is not packed as above, an error of even 77 per cent. may occur. Moreover, the results are far more concordant among themselves, and agree perfectly with those given by Kjeldahl's method when the above conditions are carried out. Substances like casein yield all their nitrogen as ammonia under these conditions, but strychnine yields only a small fraction, and the whole cannot be obtained even by Kjeldahl's method.

H. B.

Absorption of Ammonia by Acid Solutions in Nitrogen Determinations. By I. S. HAYNES (*Amer. Chem. J.*, 10, 111—113).—The absorption of the ammonia is quite complete if double the amount of acid theoretically necessary is employed, even when large

quantities of inert gases are present, and when the gases are passed rapidly through the acid, say at the rate of 90 bubbles per minute, the combustion occupying only 12 minutes. Great attention must, however, be paid to the asbestos plug in the anterior portion of the tube being packed sufficiently tightly, or particles of soda-lime will be carried forward into the acid. H. B.

Examination of Wine for Nitric Acid. By E. BORGMANN (*Zeit. anal. Chem.*, **27**, 184—187).—The method proposed by Egger (*Abstr.*, 1885, 842), for detecting the addition of water to wine by testing for nitrates with diphenylamine and sulphuric acid, is not in all respects trustworthy. Wines which on analysis give results incompatible with an addition of water are sometimes found to show the nitric acid reaction distinctly. Some of the waters of Rhenish Hesse, however, contain so much nitric acid (in one case 1 gram per litre), and the reaction will detect so small a trace (1 part in two millions of wine when Egger's concentration method is employed), that the mere rinsing of the casks with such water would introduce enough nitrate to give the reaction. On the other hand, wines to which nitrate has actually been added, have failed to give any indication of its presence after the lapse of a few months. M. J. S.

Determination of Phosphoric Acid. By F. BENTE (*Chem. Centr.*, 1887, 1241, from *Rep. anal. Chem.*, **7**, 533—534).—The low and discordant results obtained in the analysis of basic slag which were assigned by the author (*Abstr.*, 1887, 397) to the insufficient time allowed for complete precipitation, are probably brought about by the varying amount of chlorine in solution. For that reason he now employs sulphuric acid to dissolve the slag, as Brunnemann and Loges have recently done. J. P. L.

Volumetric Determination of Phosphoric Acid. By C. SCHINDLER (*Zeit. anal. Chem.*, **27**, 142—146).—The molybdenum in the yellow phosphomolybdate precipitate is determined by the author's volumetric method (p. 758), and the phosphoric acid is calculated therefrom. A precipitate of constant composition is secured by adding citric acid to the ordinary molybdate solution (15 grams to 1 litre). 50 c.c. of the nitric acid solution of the phosphate (0.5 gram of substance) is mixed with so much of a solution of ammonium nitrate (750 grams per litre), that after the addition of the molybdate the mixture shall contain 25 grams of ammonium nitrate per 100 c.c. Then for each 0.1 gram of phosphoric anhydride, 100 c.c. of molybdate is added, and the mixture is heated in a water-bath to about 58°. The precipitate is allowed to deposit for 10 minutes, the supernatant liquid is filtered, and the precipitate is washed three or four times with dilute ammonium nitrate (100 grams with 10 c.c. of nitric acid per litre). It is then dissolved in 3 per cent. ammonia, treated with 10 to 20 c.c. of Fresenius' magnesia mixture, and made up to 250 c.c. After shaking, it is filtered: 50 c.c. of the filtrate is acidified with acetic acid, diluted to 300 c.c. with hot water, and titrated with lead acetate. Comparative determinations on a variety of materials show a close agreement with the magnesia method. M. J. S.

Detection of Small Quantities of Arsenic in Fabrics, Yarn, and Wall Papers. By R. FRESSENIUS and E. HINTZ (*Zeit. anal. Chem.*, **27**, 179—182).—25 grams of the material is placed in a $\frac{1}{2}$ litre stoppered retort of Bohemian glass, and 250 c.c. of hydrochloric acid of 1.19 sp. gr. is added. The neck of the retort is bent so that the part near the bulb is inclined upward, whilst the other part slopes downward. It is connected with a condenser, which is also fitted airtight to a tubulated receiver, and this again to a Peligot's tube. The receiver and tube contain water, and are kept cold. After digestion for an hour, 5 c.c. of a cold saturated solution of ferrous chloride is added, and the liquid is slowly raised to boiling, which is continued until frothing stops the distillation. A further quantity (100 c.c.) of hydrochloric acid is then added and distilled over. The united distillates are diluted to 800 c.c., and saturated with hydrogen sulphide, first warm and then cold. The arsenious sulphide, which contains organic matter, is filtered off on an asbestos filter formed in a stop-cock funnel. After partial washing, it is treated with a solution of bromine in hydrochloric acid (1.19), and the solution, washed through with the same acid, is again distilled with ferrous chloride in an apparatus similar to the former, but smaller. The distillate now gives arsenious sulphide free from organic matter, and requiring only to be purified from sulphur. Test analyses gave satisfactory results. The residue in the retort was found to be free from arsenic.

M. J. S.

Some Methods of Separating and Determining Arsenic, Antimony, and Tin. By E. LESSER (*Zeit. anal. Chem.*, **27**, 218—221).—The oxalic acid method of F. W. Clarke (*Chem. News*, **21**, 124) gives good results. To the solution, which should be neutralised as far as possible, 35 to 40 parts of oxalic acid are added for each part of tin present. The liquid is then heated whilst being saturated with hydrogen sulphide. The precipitate is dissolved in ammonium sulphide, and the solution acidified with oxalic acid is again saturated whilst hot with hydrogen sulphide. The two filtrates which contain the tin are concentrated, mixed with ammonia, ammonium sulphide, and acetic acid, and the precipitate converted into stannic oxide for weighing. The arsenious and antimonious sulphides are dissolved from the filter by ammonium sulphide, oxidised with hydrochloric acid and chlorate, and the arsenic precipitated as magnesium arsenate, after addition of tartaric acid. The precipitate requires resolution and reprecipitation to free it from basic magnesium tartrate.

Vohl boils the strongly acid solution of the three metals, and adds sodium thiosulphate until the precipitate becomes white. The precipitate contains the arsenic and antimony. Lesser finds the separation of tin and arsenic by this method satisfactory, but that of tin and antimony inaccurate.

De Clermond and Frommel's method of separating arsenic from the other two metals by boiling the sulphides with water until they are completely converted into oxides does not give good results, as the oxides of tin and antimony are not absolutely insoluble. Neither is the separation of arsenic from antimony by strong hydrochloric acid satisfactory.

Lesser weighed his antimony as tetroxide, but recommends weighing as sulphide, for which purpose the precipitate, freed from sulphur by carbon bisulphide, is washed into a weighed porcelain crucible by ammonium sulphide, and dried in the covered crucible in the air-bath at 200—230°, for at least nine hours. M. J. S.

Separation and Estimation of Boric Acid. By H. N. MORSE and W. M. BURTON (*Amer. Chem. J.*, **10**, 154—158).—The substance, if insoluble in water, is heated with pure potash in a nickel crucible for two hours, so as just to maintain the whole in a state of fusion. The mass is extracted with hot water, which if iron is present, must amount to 100 parts for every part of potash employed, and the whole is heated on a water-bath for a considerable time; this precaution is necessary, as otherwise the iron is not completely removed, and ferric sulphate being soluble in alcohol, its presence is not admissible. The filtered solution is evaporated to 10 or 12 c.c., and after addition of a few drops of tropæolin, OO, a not too dilute sulphuric is added, until exactly neutral. The solution now containing only neutral salts of the alkalis, boric, silicic, and carbonic acids, and not exceeding 20 c.c. in volume, is dried by slowly stirring into it pure copper sulphate (free from iron and from chlorides) that has been dehydrated at 150°. The powdered mass is transferred to a filter-tube, and extracted with absolute alcohol (dried over copper sulphate) in six lots of 15 c.c. each. The alcoholic filtrate is run into a quantity of standard baryta solution, the excess of baryta is converted into the carbonate by a current of carbonic acid, and the whole is then evaporated and ignited in a platinum dish over a good burner. The residue is a mixture of barium metaborate and carbonate; the amount of boric anhydride is found thus:—as the molecular weight of boric anhydride minus the molecular weight of carbonic anhydride is to the molecular weight of boric anhydride, so is the weight of residue minus the theoretical weight of the barium carbonate obtainable from the baryta used, to the weight of boric anhydride present. The analyses quoted are exceedingly concordant and satisfactory. H. B.

Estimation of Silver in Alloys of Silver and Copper. By H. RÜSSLER (*Dingl. polyt. J.*, **267**, 570—572).—Gay-Lussac's wet assay is recommended in cases where great accuracy is required, providing that the alloy to be assayed is melted, and a sample taken from the fused mass. This is necessary, as alloys of silver and copper in solidifying do not remain homogeneous throughout, the inner and outer parts of the alloy containing different proportions of silver.

D. B.

Estimation and Separation of Metals by means of Sodium Pyrophosphate. By G. VORTMANN (*Ber.*, **21**, 1103—1106).—The behaviour of metallic salts towards sodium pyrophosphate and acetic acid can be employed as a means of separating the metals, and the pyrophosphates thus obtained, being insoluble in water, dilute acetic acid, and solutions of ammonium salts, can be made use of for quantitative determinations.

Copper salts give with sodium pyrophosphate a bright blue precipitate, soluble in excess of the reagent; on adding acetic acid, a bright blue crystalline precipitate is obtained, the precipitation is, however, incomplete, and can be entirely prevented by the addition of sodium tartrate or sodium thiosulphate.

Cadmium salts give a precipitate soluble in excess. Acetic acid reprecipitates the salt almost completely even in the cold; by evaporating to dryness and digesting the residue with water, reprecipitation is complete. The addition of sodium tartrate or thiosulphate does not hinder the precipitation.

Manganese salts yield a precipitate, soluble in excess, but completely reprecipitated by acetic acid; sodium tartrate does not prevent the precipitation.

Zinc salts behave similarly, but reprecipitation is complete only when the solution is evaporated to dryness and the residue taken up with water; sodium tartrate retards reprecipitation.

Cobalt salts give a gelatinous precipitate, soluble in excess; on shaking or heating gently, the solution becomes gelatinous but not if sodium tartrate is added. Acetic acid reprecipitates the cobalt salt. Presence of sodium tartrate does not prevent reprecipitation.

Nickel salts behave similarly, but the addition of sodium tartrate prevents the reprecipitation with acetic acid.

Ferrous salts yield a precipitate soluble in excess, but completely reprecipitated on addition of acetic acid.

Ferric salts give a precipitate soluble in excess and not precipitated by acetic acid; on addition of acetic acid and sodium sulphite, reprecipitation is complete.

Aluminium salts give a precipitate soluble in excess, but completely reprecipitated by adding acetic acid and boiling; the addition of sodium tartrate prevents reprecipitation.

Uranic salts give a precipitate soluble in excess and not reprecipitated by acetic acid.

Chromic salts give a bright green precipitate which is scarcely soluble in excess even on boiling. Acetic acid prevents the precipitation of chromic salts, but the solution becomes turbid; the addition of sodium tartrate prevents the turbidity.

From the above results it will be seen that by means of sodium pyrophosphate copper can be separated from cadmium, cobalt from nickel, manganese and zinc from ferric salts, manganese from aluminium and uranium, and ferrous salts from aluminium and uranium, possibly also from chromium and ferric salts. Cadmium, zinc, manganese, cobalt, nickel, possibly also iron and aluminium, can be estimated as pyrophosphates.

F. S. K.

Reduction with Lead. By F. STOLBA (*Chem. Centr.*, 1887, 1240, from *Listy. Chem.*, **11**, 225—226).—Under certain conditions, lead reduces iron, chromium, and tin chlorides almost as quickly and completely as zinc. Lead, however, only reduces stannic chloride to stannous chloride. Small quantities of nitric acid do not influence the reduction.

J. P. L.

Colorimetric Estimation of Minimal Quantities of Iron.

By SABANÉEFF and KISLAKOWSKI (*Chem. Centr.*, 1888, 84, from *Pharm. Zeit. Russ.*, 26, 776—777).—For the estimation of minimal quantities of iron in mineral waters, &c., the colorimetric method with ammonium sulphide leaves nothing to be desired, either from the point of rapidity or precision. It is also free from the errors which organic substances may cause in titrating iron with potassium permanganate or alkaline chromate.

J. P. L.

Determination of Iron in Iron Ores by the Tartaric Acid Method.

By L. BLUM (*Zeit. anal. Chem.*, 27, 146—151).—A source of error in the precipitation of iron by ammonium sulphide from solutions of ores containing magnesium and phosphoric acid, exists in the simultaneous precipitation of magnesium phosphate, the phosphoric acid of which subsequently comes down with the ferric oxide when the solution of the sulphide is precipitated by ammonia. With ores containing only a small amount of phosphoric acid and for technical determinations, the error can be practically got rid of by largely diluting the solution, heating it before adding ammonium sulphide, and before filtering allowing it to remain only just long enough for the ferrous sulphide to subside (about half an hour).

Fresenius points out in a footnote that a more certain way would be to precipitate the iron with most of the alumina as basic salts, before separating by ammonium sulphide in a tartrate solution, or else to allow the solution made alkaline by ammonia to remain for some time and to filter before the addition of ammonium sulphide.

M. J. S.

Estimation of Chromium in Iron or Steel in presence of Phosphorus.

By J. O. ARNOLD and H. J. HARDY (*Chem. News.*, 57, 153—155).—As the method of analysis previously described (*Abstr.*, 1880, 646) is not accurate in the presence of much phosphorus, the authors have modified it. They observed that under suitable conditions chromium is readily precipitated as a basic phosphate of constant composition, and they base the improved method on that fact. They take 2.4 grams of metal, and after the fusion make the precipitate and solution together up to 301 c.c., then 250 c.c. of the clear solution (containing the chromium from 2 grams of metal) is acidified with hydrochloric acid and boiled (no alcohol is added, the necessary reduction being effected by the nitrous gases evolved), excess of sodium phosphate is now added, then dilute ammonia in slight excess, and the whole heated until the solution is clear and colourless. The precipitate is dissolved in hydrochloric acid, carefully evaporated to dryness, redissolved by boiling with a few c.c. of hydrochloric acid and filtered. The chromium phosphate is now reprecipitated from the diluted solution by a slight excess of dilute ammonia, washed carefully, dried, and weighed as $\text{Cr}_2\text{P}_4\text{O}_{19}$. This method has given good results in the authors' hands. Titrating the chromium in the precipitated phosphate by means of permanganate gives low results.

D. A. L.

Volumetric Determination of Molybdenum and Lead. By C. SCHINDLER (*Zeit. anal. Chem.*, 27, 137—142).—Ammonium

molybdate mixed with lead acetate gives a precipitate of lead molybdate, PbMoO_4 , which is perfectly insoluble in acetic acid. An excess of the molybdate is detected by bringing a drop in contact with a solution of tannin (1—300). One part of the molybdate in 400,000 of water gives a visible yellow colour with tannin; strong solutions a blood-red. The lead acetate solution contains 40 to 50 grams (with some acetic acid) in the litre. The molybdate solution is made by dissolving 20 grams in 800 of water, adding ammonia until the turbidity disappears, and diluting until it corresponds with the lead solution in strength. To make a titration, the molybdate solution is acidified with acetic acid and diluted to 300 or 400 c.c. with hot water; a small excess of the lead solution is added, and then molybdate until a large drop of the clear, upper liquor brought in contact with a drop of the tannin solution on a porcelain plate gives a distinct orange colour. The exact strength of the lead solution should be determined by means of weighed quantities of pure ammonium molybdate, $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} + 4\text{H}_2\text{O}]$, or, if otherwise ascertained, a deduction of 0.1 c.c. of molybdate solution must be made to allow for the excess required (207Pb to 144MoO_3). The tannin solution must be freshly prepared.

M. J. S.

Determination of the Amount of Soda and Lime requisite for Purifying Water. By O. BINDER (*Zeit. anal. Chem.*, **27**, 176).—A measured quantity of the water is mixed with an excess of saturated lime-water of known strength. The mixture is warmed to between 50° and 80° , cooled, made up with boiled distilled water, filtered, and the excess of lime in the filtrate titrated with sulphuric acid, using phenolphthalein as indicator. The amount of lime required by the water is greater than that which corresponds to the temporary hardness, since magnesia as well as magnesium carbonate is precipitated both from the hydrogen carbonate and from the sulphate and chloride, and because a certain quantity of lime is consumed by free carbonic acid and by organic matters.

For the quantity of soda required, 250 c.c. of the water is evaporated to dryness with 5 c.c. of normal sodium carbonate solution. The residue is dissolved in water, filtered, and the excess of soda titrated by an acid and methyl-orange. It is advisable in practice to use 10 grams per cubic metre above the quantity thus indicated.

M. J. S.

Ash Determination. By L. REESE (*Zeit. anal. Chem.*, **27**, 133—136).—The incineration is carried on in a tube through which a rapid current of air is being drawn. Substances which are liable to intumesce and leave a difficultly combustible coal can thus be burnt in one-third to one-half of the time and at a lower temperature than would be required in a crucible. The substance is placed in a porcelain boat which is inserted into a short piece of combustion tube, narrowed at one end, and containing at that end a plug of platinum gauze to arrest any particles of ash carried off by the air current. The tube has a spiral of platinum wire round it to prevent adhesion to the outer tube in which it is placed to be heated.

M. J. S.

Quantitative Determination of Paraffin. By R. ZALOZIECKI (*Dingl. polyt. J.*, **267**, 274—279).—The principle of the author's method is the same as that on which Engler and Boehm's process is based, a precipitating agent being employed which has no solvent action on paraffin, but dissolves the accompanying impurities. It was found by experiment that paraffin is insoluble in ethyl alcohol of 75° Tralles, its solubility in amyl alcohol is diminished by the addition of ethyl alcohol, whilst the solubility does not decrease proportionately with reduction of temperature. The method, which is a simplification of the Engler and Boehm process, is as follows:—10 to 20 c.c. or grams of the paraffin under examination is mixed with five times the amount of amyl alcohol and the same volume of ethyl alcohol of 75° Tr., and the mixture kept for one hour at a temperature not exceeding 4° if possible. It is filtered through a dry filter and the residue washed with a cold mixture of 2 parts of amyl alcohol and 1 part of ethyl alcohol (70° Tr.). The paraffin is then extracted from the residue by means of ether in an apparatus illustrated in the original paper. The filter and contents are placed in a glass tube open at both ends, which is put into a wider tube. The latter is fitted into a tared flask. After extraction the flask is dried at 125° and weighed.

The method is adapted to the determination of paraffin in crude oils, in which case it is recommended to use twice the amount of mixed alcohols. By the same method, paraffin in fatty acids, neutral fats, resins, and resin oils may be determined with comparative accuracy. It is, however, inapplicable to the estimation of paraffin in waxes (beeswax, for instance), owing to their insolubility in alcohol.

D. B.

Determination of Acetone in Methyl Alcohol; Wood Spirit, and Acetone. By E. HINTZ (*Zeit. anal. Chem.*, **27**, 182—184).—Krämer's method (*Abstr.*, 1880, 826) gives good results only when the liquid under examination does not contain more than 1.5 per cent. of acetone. Liquids with a higher percentage must be diluted with water. Blank experiments are necessary to obtain a correction for the solubility of the iodides in ether, and in the case of wood spirit a blank in which the iodine is omitted must be made in order to correct for tarry matters which precipitate.

M. J. S.

Plastering of Wine. By P. CARLES (*J. Pharm.* [5], **17**, 11—14).—The volumetric and gravimetric estimations of potassium sulphate in wines often disagree. This is largely due to the modern practice of adding sulphurous anhydride in solution instead of in the gaseous state as formerly. The solution thus added may contain sulphites, and compounds are more likely to be formed in the wine which are capable of precipitating barium chloride if the wine be much exposed to the air and to acids as in the gravimetric process. In practised hands, the simple volumetric process is most satisfactory. This consists in adding standard barium chloride solution to the boiling wine, filtering a little, and testing to ascertain that no further precipitation follows the addition of either barium chloride or saturated calcium sulphate solution.

J. T.

Detection of Fahlberg's "Saccharin" in Articles of Food. By E. BÖRNSTEIN (*Zeit. anal. Chem.*, **27**, 165—168).—For detecting it in sugar, Herzfeld acidifies slightly with an acid, shakes with ether, distils the ethereal solution, fuses the residue with soda and nitre, and calculates the amount of sulphinide from a determination of the sulphuric acid. Schmitt's method depends on the formation of salicylic acid when the "saccharin" is fused with sodium hydroxide, but the absence of ready formed salicylic acid from the material under examination is an essential condition.

The author relies on the following reaction:—A solution of "saccharin" in strong (25 to 30 per cent.) potash treated with bromine drop by drop until a permanent yellow colour remains, yields on cooling a yellow, pulpy precipitate, which shows transparent, yellow prisms and needles under the microscope. Heated on platinum, it swells in vermicular forms, and leaves a bulky coal containing potash. Heated with water, it evolves bromine and slowly dissolves. The solution on cooling deposits at first yellow, transparent crystals with acute-angled edges; on concentrating the mother-liquor, white satiny plates are obtained. These substances are being further examined. 0.01 gram of "saccharin" is sufficient for recognition in this manner. A more delicate test is based on an observation of Remsen's (*Amer. Chem. J.*, 1887, 372). A minute quantity of "saccharin" heated in a test-tube with a small excess of resorcinol and a few drops of strong sulphuric acid turns yellow, red, and then deep green, and effervesces strongly from escape of sulphur dioxide. After cooling and dilution with water, an excess of alkali is added, when a solution is obtained which appears red by transmitted light, but with a strong green fluorescence. A milligram of saccharin is enough to give 6 litres of fluorescent solution. To examine an article of food by this means, the substance is exhausted with ether after slightly acidifying, best with phosphoric acid. Chocolate should first be freed from fat by light petroleum, then mixed with phosphoric acid and sand, and dried at 100° before extraction with ether. Remsen's observation relates to orthosulphobenzoic acid, but it appears that commercial "saccharin" consists to a great extent of this substance mixed with parasulphaminebenzoic acid. It is, however, highly probable that the pure sulphinide would also give the fluorescence reaction.

M. J. S.

Action of Oils on Polarised Light. By PÉTER (*Bull. Soc. Chim.*, **48**, 483—486).—The results of the examination of the effect of several oils on polarised light are given. It is proposed to determine qualitatively the nature of oils by their action on polarised light, and to this end the author is engaged in making an analytical table. The results yielded by the polariscope, and by a determination of density, and of the heat developed when the oil is mixed with sulphuric acid, are more trustworthy than colour reactions, and are more readily obtained (compare also Bishop, this vol., p. 388).

N. H. M.

Apparatus for the Extraction of Fat in the Cold. By O. FOERSTER (*Zeit. anal. Chem.*, **27**, 173—175).—The substance is placed

in a filter-tube terminating below in a glass worm, the whole being surrounded with a glass water-jacket, and ground into the neck of a flask. A side-tube conveys the vapour from the flask to a second worm above the substance, where it is condensed and cooled before it falls upon the material. Figures of the apparatus (which is made by Müller, of Bonn) are given. M. J. S.

Test for Acetanilide. By F. FLÜCKIGER (*Chem. Centr.*, 1888, 26; from *Apoth. Zeit.*, 1887, 410).—If two parts of acetanilide moistened with chloroform is rubbed up with one part of potash, transferred to a flask and gently heated, phenyl isocyanide is formed, which can be readily detected by its peculiar and unmistakable odour. The heat must not be allowed to rise too high, for at 167° phenyl isocyanide boils with decomposition, and at 200—220° it is converted into its isomeride, benzonitrile, which under these circumstances would be converted into a benzoate and ammonia. J. P. L.

Separation of Resins. By G. KLIEBHAN (*Chem. Centr.*, 1888, 87, from *Pharm. Zeit. Russ.*, 26, 777—779).—The relative solubility in various solvents, and the behaviour towards acetic, sulphuric, and nitric acids, boiling aqueous soda, and ammonia, afford the best means of separating the different resins. In the following experiments, the powdered resins were treated with three times their volume of the solvent at a temperature of 29—30°. In boiling water, colophony forms a half-melted mass; shellac, mastic, elemi, and dammar agglomerate; sandarach, copal, and amber remain unchanged. In alcohol, mastic, shellac, sandarach, and colophony are soluble; elemi soluble with difficulty; dammar and amber insoluble; copal agglomerates. In ether, dammar, colophony, mastic, elemi, and sandarach are readily soluble; amber and shellac insoluble; copal swells up. Carbon bisulphide dissolves dammar and colophony readily; mastic, elemi, and sandarach with difficulty; amber and shellac not at all. Benzene dissolves dammar, mastic, and colophony; sandarach and elemi with difficulty; whilst amber, shellac, and copal are insoluble. Light petroleum dissolves dammar and mastic readily; colophony, elemi, and sandarach with difficulty; amber, copal, and shellac not at all. Acetic acid causes colophony to swell, but is without action on the other resins. Sulphuric acid dissolves all resins, but causes charring and decomposition; dammar, on the other hand, when treated with sulphuric acid, becomes bright red. Nitric acid colours mastic and sandarach bright yellow; elemi, a dirty yellow. Aqueous soda dissolves shellac readily; colophony with difficulty, but is without solvent action on the others. Colophony dissolves readily in strong ammonia; mastic, sandarach, and copal swell up before dissolving; whilst amber, dammar, shellac, and elemi remain unchanged. J. P. L.

Valuation of Indigoes. By C. RAWSON (*Chem. News*, 57, 7—8, 19—20, 29—30, 34—36).—As much diversity of opinion exists in connection with the valuation of indigoes, the author has investigated the subject and examined the various methods employed. The sample

for analysis should consist of small pieces from each lump in the lot sent for analysis, finely ground, and all passed through a sieve. 1 gram of the finely-powdered indigo is mixed with an equal weight of ground glass and gradually added with stirring to 20 c.c. of sulphuric acid (sp. gr. 1.845), it is now placed for one hour in a steam-bath at 90°. The indigotin is then completely dissolved, and the sulphindigotic acid formed is diluted to 1 litre. Of all the methods of estimating indigotin depending on oxidation, the author prefers the permanganate method; a mere titration, however, only gives an approximate estimate, inasmuch as the impurities soluble in dilute acids are also attacked, and so the results are high; the following method is recommended to eliminate this error:—50 c.c. of the filtered sulphindigotic acid is mixed with 50 c.c. of water and 32 grams of sodium chloride; sodium sulphindigotate being almost insoluble in strong salt solution separates, and after two hours is collected, washed with salt solution (sp. gr. 1.2), dissolved in hot water, and when cool acidified with 1 c.c. of sulphuric acid, then diluted to 300 c.c., and titrated with permanganate; a small correction has to be made for the sulphindigotate retained by the salt solution; the results agree very closely with the combined percentages of indigotin and indigo-red.

The hyposulphite method (Abstr., 1881, 310) is fully described and studied; the author finds that neither indigo-gluten, indigo-brown, nor indigo-red have any appreciable effect on the results obtained by this method. Ferric salts, however, cause high results, and in fact a method is suggested for estimating ferric iron by means of hyposulphite.

The sublimation method (Lee, Abstr., 1884, 1438) is inaccurate, inasmuch as pure indigotin suffers decomposition under this treatment, whilst in ordinary indigo many of the impurities are affected, and, therefore, in the first instance the results are too low, and in the second too high.

Methods based on the reduction of indigo in alkaline solutions are not as accurate as is generally supposed; a modified, and apparently tedious, ferrous sulphate and sodium hydroxide method (Crace-Calvert's method) is described in detail, but the following is recommended as most trustworthy:—A gram of finely-powdered indigo is made into a paste with water and placed in a flask with 500 to 600 c.c. of lime-water, the flask is closed with an india-rubber stopper bored with four holes, one carrying a syphon, another a tap-funnel, the remaining two serve for the ingress and egress of a current of coal-gas, the whole is heated at 80°; 100 to 150 c.c. of sodium hyposulphite (Na_2SO_3 , not thiosulphate) solution (5 times as strong as the solution used in the acid method) introduced and kept near the boiling point for half an hour, allowed to settle, and 500 c.c. of the clear liquid syphoned off, oxidised by aspirating air through it for 20 minutes, an excess of hydrochloric acid added, and the precipitate of indigotin and indigo-red washed and weighed. The liquid remaining in the flask is measured, and the results calculated on the whole quantity. If the proportion of indigo-red is required, the filter and precipitate are extracted with alcohol in an extraction apparatus, when the red passes into solution.

D. A. L.

Allen's Method for the Detection of Hop-substitutes in Beer. By J. O. ARNOLD (*Chem. News*, **57**, 33).—In reference to Allen's method (Abstr., 1887, 1146), the author has not succeeded in removing completely the bitter principle of the hop from beer by precipitation with either basic or normal lead acetate. D. A. L.

Precipitation of Hop-bitter by Lead Acetate. By A. H. ALLEN (*Chem. News*, **57**, 53—54).—A rejoinder to Arnold (see preceding Abstract). The author disclaims the discovery of the process in question, and acknowledges that lead acetate cannot be relied on for the complete precipitation of hop-bitter. He has noticed that solutions which were bitter when the excess of lead was removed from the solution by means of hydrogen sulphide, lost all bitterness when sulphuric acid was employed instead of hydrogen sulphide.

D. A. L.

Precipitation of Hop-bitter by Lead Acetate. By A. H. ALLEN (*Analyst*, **13**, 43).—Contrary to his former experience, the author now finds that lead acetate cannot be relied on for the complete removal of the bitter principle from an infusion of hops. In most cases it succeeds fairly well, but in other cases the residue from the filtrate has a strongly marked bitter taste. By using excess of sulphuric acid instead of hydrogen sulphide for the removal of the lead, the traces of hop bitter left in the filtrate are got rid of during the evaporation. Foreign bitters can, however (according to Adams), always be detected, with the exception of camomile, the bitter of which is precipitated by lead acetate.

M. J. S.

Precipitation of Hop-bitter by Lead Acetate. By W. JOHNSTONE (*Analyst*, **13**, 6—7).—The author, having examined a sample of hops of undoubted purity, found that the filtrate from the lead precipitate left a bitter residue. No details are given (comp. Allen, Abstr., 1887, 1146).

M. J. S.

Detection of Proteïds in Urine. By S. H. C. MARTIN (*Brit. Med. Journ.*, **1**, 1888, 842—844).—The tests ordinarily applied for the detection of proteïds in urine in clinical work do not distinguish between the numerous substances included under that name. The object of the present paper is to discuss the more modern methods of the separation and detection of proteïds, as applied when those substances occur in the urine. It is necessary that the proteïd should be first obtained free from the other constituents of the urine. This is done by saturating the fluid with ammonium sulphate; by this means, albumins, globulins, and albumoses are precipitated. The precipitate is collected, washed with saturated solution of ammonium sulphate, and redissolved by the addition of water; the presence of a small amount of ammonium sulphate in this solution does not interfere with their distinctive properties. *Albumins* may be recognised in this solution by the fact that they are not precipitated by saturation with magnesium sulphate, and that they coagulate by heating their solutions to about 73°. Egg albumin is coagulated by ether, serum albumin (the proteïd which most frequently occurs in urine) is not. *Globulins*

on the other hand, are precipitated by saturation with magnesium sulphate; serum globulin, which is practically the only globulin that is ever present in urine, coagulates by heat at about 75° . Of *albumoses*, that which most frequently occurs in urine is heteroalbumose. This is precipitated by heat even when no acetic or other free acid is added, whilst albumins and globulins are not; this precipitate comes down at $43-50^{\circ}$, and is soluble in a few drops of weak acid; coagulated albumin or globulin is not. This substance also gives the characteristic nitric acid test for albumoses, and the biuret reaction. It is moreover precipitated by saturation with magnesium sulphate. If other albumoses or globuloses are present, the various distinctive tests as described by Kühne and Chittenden must be applied. The only method for determining the presence of *peptones* in urine is the fact that they are not precipitated by saturation with ammonium sulphate; any proteid remaining in solution after the precipitation of other proteids by saturation with that salt must be peptone; it may be identified in such a saturated solution by the xanthoproteic and biuret reactions.

W. D. H.

Action of Bleaching Agents on Writing Ink. By R. IRVINE (*J. Soc. Chem. Ind.*, 6, 807—808).—The author made a series of experiments to ascertain whether it is possible to tell the age of writing, and if writing has been executed at one and the same time, and if so, at what time. He selected writing one day, six months, 12 months, 2 years, 6 years, 14 years, and 22 years old, and exposed these writings to the action of a very dilute solution of bleaching powder, sp. gr. 1.001. In six minutes, the newly-written matter had disappeared; in from nine to 12 minutes, the writing of six months ago had disappeared; in 20 minutes, the writing of two years had partly disappeared, whilst in a like time the writing of six years ago was not greatly affected, of 14 years ago very slightly, and of 22 years hardly at all. Hydrogen peroxide acts more slowly but gives more definite results. When writing ink is thus bleached, most of the iron contained therein remains mordanted with the fibres of the paper, consequently writing so tampered with can be restored by the application of gallic or tannic acid. In determining the age of any particular writing, the following precautions should be observed:—(1) The inks must be those known as ordinary writing inks prepared from iron and chromium salts and galls. (2) Writing dried by means of blotting-paper is more easily removed than writing which is allowed to dry on the surface of the paper. (3) The bleaching solution must be exceedingly dilute, otherwise the action is so rapid and powerful, that both old and new writings are removed almost simultaneously. (4) The action must be carefully watched so as not to be too long continued. (5) Very old writing which has become brown by age, although it resists the action of weak solutions of bleaching powder and hydrogen peroxide, will show signs of giving way almost instantly when acted on by dilute nitric, hydrochloric, or oxalic acids.

D. B.

General and Physical Chemistry.

Influence of Pressure on the Index of Refraction of Water for Sodium Light. By L. ZEHNDER (*Ann. Phys. Chem.* [2], 34, 91—121).—This investigation was carried out principally with the view of deciding whether the so-called specific refraction or some similar expression was truly a constant. Gladstone and Dale (*Phil. Trans.*, 153, 317) have investigated the effect of change of pressure on the index of refraction of liquids, and they came to the conclusion that when D is the density of the liquid, the quantity $(\mu - 1)/D$ is a constant. Landolt (*Ann. Phys. Chem.*, 123, 595) arrived at a similar conclusion. Rühlmann (*ibid.*, 132, 1) and Wüllner (*ibid.*, 133, 1) came to the conclusion that it was not perfectly constant. According to Jamin (*Ann. Chim. Phys.*, 52, 163), the quantity $(\mu^2 - 1)/D$ is a constant. Mascart (*Ann. Phys. Chem.*, 153, 154) denied the constancy of this quantity, and Quincke (*ibid.* [2], 19, 401) confirmed Gladstone and Dale's conclusion. L. Lorentz (*ibid.* [2], 11, 70) and H. A. Lorentz (*ibid.* [2], 9, 641) independently arrived at the result that $(\mu^2 - 1)/(\mu^2 + 2) \cdot 1/D$ was constant.

The author, as the results of a series of observations carried out with minute precautions, arrives at the conclusion that Gladstone and Dale's result, $(\mu - 1)/D = \text{constant}$, is a very close approximation to the truth, and that the other relations are not.

G. W. T.

Spectra of Oxygen. By J. JANSSEN (*Compt. rend.*, 106, 1118—1119).—Observations on the Pic du Midi show that the indistinct absorption-bands in the oxygen spectrum (Abstr., 1886, 749) can be seen in the solar spectrum if the atmospheric layer through which the sunlight passes is of sufficient diameter. The existence of these bands, and the law that their intensity is proportional to the product of the diameter of the layer of oxygen into the square of the density of the gas, is confirmed by a series of observations extending from normal pressure to a pressure of 100 atmos. with tubes varying from 0.42 to 60 metres in length. The author calculates that these bands should be just visible with a layer of liquid oxygen 4 to 5 mm. in thickness; and Olzewski has actually observed them with a layer of 7 mm. in thickness.

C. H. B.

Spectrum of Gold. By E. DEMARÇAY (*Compt. rend.*, 106, 1228—1230).—The lines at 5230, 4437, 4338, and 4064, which Boisbaudran observed in the spectrum of gold, but which Krüss attributes to the presence of platinum and palladium, are not really due to these metals. They are visible although all the other lines of platinum and palladium are absent, and they do not actually coincide with

any lines of these metals. The lines 5230, 4437, and 4064 are undoubtedly due to gold, but the author was unable to observe the line 4338 in a condensed spark spectrum.

Boisbaudran has since found that the line 4338 is only visible with concentrated solutions of gold chloride, and it may be due to a non-metallic element.

C. H. B.

Application of the Method of High Interferences to Quantitative Spectrum Analysis. By H. EBERT (*Ann. Phys. Chem.* [2], **34**, 39—90).—The author points out that the researches of Fizeau and Foucault (*Ann. Chim. Phys.* [3], **26**, 138, and [3], **66**, 429; *Compt. rend.*, **21**, 1155, **26**, 680, and **54**, 1237), Billet (*Compt. rend.*, **67**, 1000), Mascart (*Ann. de l'école Normal* [2], **1**, 57), Ketteler (*Beobachtungen über die Farbenzerstreuung der Gase*, Bonn, 1865), Müller (*Ann. Phys. Chem.*, **150**, 86), the author himself (*ibid.* [2], **32**, 337), and Michelson and Morley (*Amer. J. Sci.* [3], **34**, 427), on interference with large difference in length of path, show that although the possibility of interference is limited by conditions depending on the change in the vibrations of the luminous particles, the limits are wide ones, and the last-named authors observed cases of interference with a difference in length of path of as much as 200,000 times the wave-length. Müller was the first who applied this to the study of the source of light itself.

The method is very suitable for investigating small alterations in the refrangibility of lines in the spectrum. With light corresponding with the green mercury line, the author has obtained interference phenomena with a difference in length of path 80,000 times the wave-length, and as a shifting in one of the bands of one-tenth its thickness can be observed, an alteration of $1/800000$ of the wave-length, or $1/800$ of the distance between the two sodium lines can be determined.

The most homogeneous lines in the spectrum are formed by a number of component vibrations which differ very little in wave-length, and the amplitudes of which are a definite function of the wave-length; alterations in the interference bands simply giving evidence of changes in the mean wave-length.

The determination of the greatest difference in length of path for which interference bands are obtained gives a measure of the time during which the luminous molecules maintain their vibrations unchanged, because two rays from the same luminous particle will interfere only if the vibration is the same at the moment of emission of each of the rays.

Wiedemann has considered this question (*Ann. Phys. Chem.* [2], **5**, 503; *Phil. Mag.* [5], **7**, 77), and has shown that the value of this maximum length of path is intimately connected with the mean length of the molecular free path, and in the case of sodium vapour the method gave a number of the same order of magnitude as that calculated from the kinetic theory of gases.

An increase in the density of the gas will narrow the limits within which interference is possible, as after contact between two molecules the vibrations will be altered, so that two rays to interfere must both

come from a molecule during the interval between two encounters. Lippich has also shown (*Wien. Ber.*, 82) that an increase of temperature has the same effect, but the increase of the density is of greater importance, as is easily seen, and was pointed out by Wiedemann in the paper referred to. This physicist has applied the method to the investigation of the pressure at the surface of the sun and stars (*Phil. Mag.* [5], 10, 123).

It is clear from these considerations that the method can only give a lower limit for the duration of the undisturbed vibration of a free molecule. An important question to be determined is the influence exerted by the breadth of the spectrum line on the greatest length of path for which interference is possible.

Müller, in the paper referred to, shows that the finite breadth of a spectrum line gives rise to secondary systems of interference bands, causing an alteration in the clearness of the primary bands, and he shows by theoretical reasoning that the effect of gradually widening the line, maintaining the difference in length of path constant, has the same effect as gradually increasing the difference in length of path while maintaining the breadth constant. In confirmation of this he states that when a bead of salt is gradually plunged deeper into a bunsen flame, thus increasing the quantity of vapour, the lines become wider. The author has been unable to observe this alteration, and believes that Müller must have been mistaken, as the effect could not possibly be sufficient to be appreciated by the eye. The author does find an increase in clearness when the bead is plunged deeper into the flame, but only when it passes into the cooler interior portion, so that the quantity of vapour is diminished, and therefore the spectrum line becomes more homogeneous.

With regard to the limits of the method, the author shows that it is impossible to follow the shifting of the bands due to broadening of the line for much more than the width of the band, but the extent to which the widening of a line for a given difference in length of path can be observed is only limited by the thinness of the plates used to obtain the fringes; and on the other hand, by increasing the thickness of the plates, the earlier stages of the widening process can be observed.

The authors made experiments with beads consisting of salts of lithium, potassium, strontium, and sodium. When the bead first touched the outside of the flame the illumination was feeble, and the interference bands became sharply defined. As the bead was plunged more deeply into the flame the bands became less distinct, and the illumination of the field of view increased, the lines being widened and the light becoming less homogeneous. The depth to which the bead had to be plunged into the flame to cause complete disappearance of the bands was greater for the less fusible salts, and for those which gave the least homogeneous light. When the bead reached the cool interior portion of the flame, the bands reappeared. This alternate appearance and disappearance of the bands are in the author's opinion the explanation of the alternation described by Müller.

As the illumination gradually increased, the bands appeared to remain constant in position until at a certain point, corresponding with

the maximum formation of vapour, they were suddenly shifted. This sudden widening of the spectrum line may be compared with some somewhat similar phenomena observed by Cornu (*Ann. Chim. Phys.* [6], 7, 5).

The displacement of the bands was in the same direction, but not of the same amount for all the lines of the spectrum which were observed. An increase in the quantity of vapour caused a displacement indicating a decrease in the refrangibility of the widened line, so the widening was greater towards the least refrangible end. The displacement was not perceptibly altered by altering the thickness of the plate, showing that it is independent of the difference in the length of path, and depends only on the variation in brightness of the different constituent portions of the band.

With regard to the causes of the widening of the line, as the bead was gradually introduced into the flame, a change must take place (1) in the thickness of the luminous layer, (2) in the temperature, (3) in the density of the luminous vapour, (4) in the nature and energy of chemical decomposition. As a result of these, there would also be a variation in the intensity of illumination, but the author's previous researches (*Ann. Phys. Chem.* [2], 32, 337) have shown that this by itself does not alter the wave-length. The thickness of the layer was limited by the thickness of the mantle of the flame, which was about 8 mm., and within these limits its variation was found to be without influence on the mean refrangibility of the spectrum line. Alteration in the temperature did not cause any displacement in the bands, although considerable ranges of temperature were obtained, and the author concludes from his experiments that spectrum lines when beginning to widen through increase of temperature, until a certain breadth has been passed, do not undergo a change in mean refrangibility of more than a millionth part within the limits of the experiments, in which the temperature was increased by about one-third of its lowest value. The author arrives at the conclusion that the observed asymmetric widening of the lines is due entirely to the increase in the density of the vapour.

With regard to the influence of the chemical decompositions, he finds that if it exists at all it must be exceedingly small.

G. W. T.

Relation between the Constitution and Specific Rotatory Power of Organic Compounds. By B. SOROKIN (*J. pr. Chem.* [2], 37, 320—333).—The author finds that the same solvent produces identical changes in the specific rotatory power of closely related organic compounds. When, for example, the anilide of dextrose is dissolved in a 90 per cent. solution of ethyl alcohol, $[\alpha]_D = -44.11^\circ$, whilst for a solution in methyl alcohol $[\alpha]_D = -48.73^\circ$. The toluidine of dextrose in a 90 per cent. solution of ethyl alcohol gives $[\alpha]_D = -38.80^\circ$, whilst a solution in methyl alcohol shows $[\alpha]_D = -43.88^\circ$. The combination of an aniline or toluidine molecule with a molecule of dextrose produces identical changes in its optical activity. Tables showing the specific rotatory power of salicin, helicin, and other related substances are given.

G. T. M.

Conduction of Electricity through Gases. By R. NAHRWOLD (*Ann. Phys. Chem.* [2], **34**, 170—172).—Narr (this vol., p. 397) ascribes to the author the statement that the molecules of a gas are incapable of receiving a static charge. This the author says is incorrect. He concluded from his experiments that it was impossible to give an electrostatic charge to a mass of gas, but drew no conclusion as to the possibility of separate molecules becoming charged, which is quite possible, as the charge of the molecules might very possibly be dissipated before an observation could be made, either by dissociation or otherwise.

He also states that although in an earlier paper than the one quoted by Narr he alluded to the possibility of the charge on a body surrounded by a gas being dissipated by the action of dust particles, he inclines to the belief that conduction does actually take place through gases, even when no dust particles are present; and he quite agrees with Narr that his investigations leave it an open question.

G. W. T.

New Apparatus for Electrochemical Research. By N. v. KLOBUKOFF (*J. pr. Chem.* [2], **37**, 375—381).—The author describes and figures a “stopper” rheostat and an electrode holder, the chief feature in both being that contact is made by means of mercury.

A. G. B.

Alternate Currents and Electrolytes. By S. SHELDON (*Ann. Phys. Chem.* [2], **34**, 122—138).—Two essentially distinct methods are in use for determining the electrical resistance of liquids, namely, by means of constant currents, and by means of alternating currents. In order to compare the two methods, the author made a series of measurements by both methods of the resistances of dilute solutions of potassium chloride, sodium chloride, potassium sulphate, and magnesium sulphate, of nine different degrees of concentration. In every case, the results obtained by the two methods were closely concordant, and the author concludes that both the methods, if properly carried out, are capable of giving equally good results, but he decides in favour of the alternate current method, on the grounds of simplicity and convenience.

G. W. T.

Electrolytic Formation of Persulphuric Acid and Hydrogen Dioxide at the Anode. By F. RICHARZ (*Ber.*, **21**, 1669—1674, and 1682—1683; compare this vol., p. 12).—A reply to Traube (this vol., p. 210).

F. S. K.

Constitution of Peroxides. By F. RICHARZ (*Ber.*, **21**, 1675—1681).—A reply to Traube's theory of the “oxygen molecule-compounds” (this vol., p. 210), in which the author endeavours to show that Helmholtz's electrochemical theory explains the behaviour of ozonides and antozonides (peroxides) without the aid of any new hypothesis.

F. S. K.

Magnetism of Organic Compounds. By S. HENRICHSEN (*Ann. Phys. Chem.* [2], **34**, 180—221).—The substances selected by the author for his experiments were all of the fatty series, these com-

pounds being chosen because of the large number of homologous series and isomeric compounds which they contain, and also because a very large number of them can be obtained in a state of purity with very little trouble and expense. The researches were all made with liquids, as being easier to work with than either gases or solids. The author found that—1. All the substances experimented on were diamagnetic. 2. For every CH_2 -group introduced into the formula, the molecular magnetism increases by a quantity the mean value of which is 16.32 times that of the molecular magnetism of water. 3. The values of the molecular magnetism are equal for isomeric and metameric substances, provided the nature of the union is the same in each substance. 4. The molecular magnetism depends on the manner in which the atoms are united. A double bond appears to diminish the molecular magnetism. 5. The specific magnetism of primary and normal compounds is greater than that of secondary and iso-compounds, similarly it is greater for acids than for the corresponding ethereal salts. 6. By making certain assumptions the values of the atomic magnetism of the individual elements may be calculated from the experimental data. The values obtained are—

H.	O'.	O''.	C'.	C''.	Cl.	Cl''.	Cl'''.
9	129	-17	145.2	98	282	249	218
	Cl''''.	Br.	Br''.	Br'''.	I.	I''.	S.
	194	413	374	334	642	577	284

7. The values of the atomic magnetism of the halogens decrease as the number of atoms increases (the number being indicated by the dashes below the symbols in the table).

The nature of the assumption under which the results in (6) were obtained may be illustrated by giving the method of obtaining them for oxygen in single or double union respectively:—Consider compounds containing only carbon, oxygen, and hydrogen, namely, the alcohols, aldehydes, acids, and ethereal salts. The observations give the value of the molecular magnetism for each of these groups, and also the value for CH_2 ; four equations are therefore obtained which will serve to determine four quantities. Let it now be assumed that in these compounds all the carbon- and hydrogen-atoms have the same molecular magnetism, but that the value for oxygen united by one bond to carbon, O', differs from that of O'', oxygen united by two bonds. The alcohols can then be represented by the formula $n(\text{CH}_2)\text{HO}'$, the aldehydes by $n(\text{CH}_2)\text{O}''$, and the acids and compounds of alcohol radicles by $n(\text{CH}_2)\text{O}'\text{O}''$. The value for O' can then be determined directly as follows:—

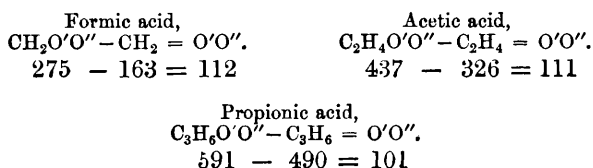
$$\begin{array}{l} \text{Aldehyde,} \\ \text{C}_2\text{H}_4\text{O}' - \text{C}_2\text{H}_4 = \text{O}'' \\ 307 - 326 = -19 \end{array}$$

$$\begin{array}{l} \text{Isobutaldehyde,} \\ \text{C}_4\text{H}_8\text{O}'' - \text{C}_4\text{H}_8 = \text{O}'' \\ 640 - 653 = -13 \end{array}$$

$$\begin{array}{l} \text{Acetone,} \\ \text{C}_3\text{H}_6\text{O}'' - \text{C}_3\text{H}_6 = \text{O}'' \\ 473 - 490 = -17 \end{array}$$

$$\begin{array}{l} \text{Valeraldehyde,} \\ \text{C}_5\text{H}_{10}\text{O}'' - \text{C}_5\text{H}_{10} = \text{O}'' \\ 797 - 816 = -21 \end{array}$$

From the previous determination of the value of C_2H_5 , the most probable value is found to be $O'' = -17$, the negative sign indicating that doubly-bound oxygen is paramagnetic. Again—



The most probable value is—

$$\begin{array}{rcl}
 & O'O'' & = 112 \\
 \text{And we had.} & O'' & = -17 \\
 \hline
 \text{Therefore....} & O' & = 129
 \end{array}$$

G. W. T.

Specific Heats of Liquid Carbon Compounds. By R. SCHIFF (*Zeit. physikal. Chem.*, **1**, 376—390; compare Abstr., 1887, 6).—The author has extended his investigations to fresh series of compounds, and obtained results similar to those previously arrived at. In each case, the mean specific heat between the temperatures t and t' may be expressed by $C_{t-t'} = a + b(t + t')$, or the true specific heat by $K_t = a + 2bt$, the coefficient b having a practically constant value for any homologous series, and a having either a constant value or increasing regularly with the molecular weight. The following table gives the results:—

	$K_t =$
For methyl chloracetate	0.3747 + 0.00038t
„ ethyl „	0.3900 + 0.00038t
„ propyl „	0.4067 + 0.00038t
„ allyl „	0.3888 + 0.00038t
„ methyl dichloracetate	0.3032 + 0.00038t
„ ethyl „	0.3215 + 0.00038t
„ propyl „	0.3335 + 0.00038t
„ allyl „	0.3244 + 0.00038t
„ methyl trichloracetate	0.2592 + 0.00038t
„ ethyl „	0.2778 + 0.00038t
„ propyl „	0.2892 + 0.00038t
„ allyl „	0.2806 + 0.00038t
„ allyl acetate and isobutyrate..	0.4305 + 0.00088t
„ allyl propionate, butyrate and valerate	0.4330 + 0.00088t
„ allyl benzoate	0.3732 + 0.00075t
„ ethyl and propyl oxalate	} 0.4199 + 0.00066t
„ „ „ malonate ...	
„ allyl oxalate.....	0.4122 + 0.00066t
„ isobutyl oxalate	0.4274 + 0.00066t
„ isoamyl „	0.4354 + 0.00066t
„ ethyl and propyl succinate ...	0.4391 + 0.00066t

	$H_t =$
For allyl succinate.....	0.4323 + 0.00066t
„ isobutyl succinate	0.4421 + 0.00066t
„ isoamyl „	0.4493 + 0.00066t
„ aniline and orthotoluidine. . .	0.4706 + 0.00070t
„ dimethylaniline	0.4018 + 0.00092t
„ diethylaniline	0.4343 + 0.00092t
„ chlorbenzene	0.2988 + 0.00074t
„ chlortoluene	0.3160 + 0.00074t
„ benzyl chloride	0.3225 + 0.00074t.

H. C.

Molecular Heats of Gaseous Substances. By H. LE CHATELIER (*Zeit. physikal. Chem.*, **1**, 456—458).—The author finds from the determinations of Wiedemann, that the specific heats of gaseous substances may be represented within the limits of experimental error by the equation $C = 6.8 + \alpha (273 + t)$, for temperatures below 200° , where C is the true specific heat at constant pressure, and α a coefficient depending on the nature of the gas, and having a higher value the more condensed the molecule. From this it would follow that as the temperature approaches the absolute zero, the molecular heats of gases and vapours would more and more approximate to the same limiting value, but in how far this may be considered a true law the experimental data are insufficient to determine. From the author's own experiments, he finds that the relation holds good for carbonic anhydride at 2000° , but for water-vapour at 3300° it no longer holds, probably owing to partial dissociation having already occurred.

H. C.

Air Thermometer. By L. CAILLETET (*Compt. rend.*, **106**, 1055—1057).—A description of a modified form of air thermometer at constant volume, the gas employed being hydrogen. The upper part of the manometer tube is vacuous, and hence the correction for atmospheric pressure is eliminated. The pressure is adjusted by means of a movable reservoir of mercury, which can be cut off from the manometer tube by a screw tap. The point of constant volume is indicated by a platinum wire, which is connected with an electric current in such a way that when the mercury in the manometer touches the wire the circuit is completed, and a bell rings. The space between the bulb and the zero point, which contains hydrogen at an unknown temperature is only 0.006 of the volume of the bulb. The hydrogen thermometer and the mercurial thermometer agree between -30° and $+50^\circ$.

C. H. B.

Air Thermometers. By CRAFTS (*Compt. rend.*, **106**, 1222—1225).—The author, like Cailletet (preceding Abstract), employs electrical connections as a means of adjusting the mercurial column in the manometer to zero, and he also makes use of an electrical stopcock, which cuts off the mercury as soon as the latter touches the platinum wire which marks the zero point. In accurate work, the whole of the mercury in the manometer and the stem of the thermometer should be immersed in melting ice.

C. H. B.

Latent Heat of Vaporisation of Volatile Substances. By J. CHAPPUIS (*Compt. rend.*, **106**, 1007—1008).—Cailletet and Mathias's determinations of the density of sulphurous anhydride (*J. de Phys.* [2], **6**, 414), together with Regnault's determinations of the maximum tensions of this substance between -30° and $+65^{\circ}$, make it possible to calculate the latent heat of vaporisation of the liquid by means of the well-known formula, and the value thus obtained, 91.2 Cal. at 0° , agrees with the author's direct determination, 91.7 Cal. (Abstr., 1887, 627).

In the case of carbonic anhydride, direct experiment gives 56.25 Cal. at 0° . The value calculated from Sarrau's data is 55.95 Cal.; from the curves given by Cailletet and Mathias (*J. de Phys.* [2], **5**, 549), 57.48; and from their equation for the variation of the latent heat of carbonic anhydride with the temperature, 56.75 Cal. C. H. B.

Measurement of the Latent Heat of Vaporisation of Liquefied Gases. By E. MATHIAS (*Compt. rend.*, **106**, 1146—1148).—The liquefied gas is contained in a copper receiver gilded externally, from which it escapes through a serpentine metal tube of narrow diameter, the whole being placed in a Berthelot's calorimeter. During the evaporation of the liquid, which is regulated by means of stopcocks, the temperature of the water is kept within 0.05° of the initial temperature by the gradual addition of sulphuric acid of known strength, care being taken to ensure rapid and perfect admixture. The decrease in the weight of the metal receiver gives the quantity of liquid which has evaporated, and the amount of acid added gives the quantity of heat required to keep the water at the initial temperature, or, in other words, the quantity of heat absorbed by the volatilisation of the liquefied gas.

Experiments with sulphurous anhydride show that the latent heat of vaporisation diminishes as the temperature rises. C. H. B.

Calorimetry at Constant Temperature. By A. D'ARSONVAL (*Compt. rend.*, **106**, 1225—1226).—The author has for some time utilised the evaporation of ethyl chloride to compensate for the heat developed by the animals in thermo-physiological experiments. The water in the calorimeter is thus kept at the initial temperature, and the quantity of heat developed is calculated from the amount of ethyl chloride volatilised. (Compare Mathias, preceding Abstract.)

C. H. B.

Heat of Formation of Aniline. By P. PETIT (*Compt. rend.*, **105**, 1087—1089).—Nitrobenzene is completely converted into aniline in a few minutes by the action of chromous oxide at the ordinary temperature. This reaction was carried out in the calorimeter by mixing nitrobenzene with a measured quantity of a standard solution of chromous chloride containing free hydrochloric acid. The heat of oxidation of chromous chloride has been determined by Recoura, and the heat of formation of aniline hydrochloride by Berthelot. C_6 diamond + H_7 gas + N gas = C_6H_7N liquid absorbs -12.4 Cal. Aniline was also burnt in oxygen in the calorimetric bomb. Only a very small quantity of nitrogen oxides is formed. The heat of combustion for

1 gram is 8.794 Cal.; for a gram-molecule at constant volume 817.8 Cal., at constant pressure 818.5 Cal. C_6 diamond + H_2 gas + N gas = C_6H_7N liquid absorbs -13.0 Cal.

The two values agree well.

C. H. B.

Thermochemistry of Diazo-derivatives. By L. VIGNON (*Compt. rend.*, **106**, 1162—1165).—The determinations were made by taking advantage of the fact that in dilute solutions the formation of the diazo-derivatives is complete, and is not complicated by secondary reactions. Moreover, if the temperature is below 10° , some time elapses before the decomposition of the diazo-derivative becomes appreciable. Dilute solutions of hydrochloric acid, aniline, or orthotoluidine, or paratoluidine, and pure sodium nitrite were mixed in the calorimeter, and the following results were obtained:—

Diazobenzene chloride	+31.4 Cal.
Orthodiazotoluene chloride	+33.6 "
Paradiazotoluene chloride	+33.1 "

The heats of formation of aniline and toluidine hydrochlorides not yet having been determined, the heats of formation of the diazo-derivatives from their elements cannot be accurately calculated, but if the heat of neutralisation of nitrous acid by soda is taken as equal to the heat of neutralisation by baryta, the following values are obtained:—

Diazobenzene chloride	A — 44.0 Cal.
Orthodiazotoluene chloride	B — 41.8 "
Paradiazotoluene chloride	C — 42.3 "

Where A, B, and C, are the heats of formation of the hydrochlorides of aniline, orthotoluidine and paratoluidine, respectively. The formation of the diazo-derivatives themselves is undoubtedly endothermic, a result which explains their instability and the necessity for cooling the reagents during their formation. The development of heat which is observed is due to the formation of water and sodium chloride.

C. H. B.

Heat of Combustion of Coals from the North of France. By SCHEURER-KESTNER (*Compt. rend.*, **106**, 1092—1094, 1160—1161, 1230—1231).—The coal, in small fragments, was burnt in a rapid current of oxygen in a Favre and Silbermann's calorimeter. Under these conditions, combustion is much more complete than if the coal is finely powdered. Twenty-one samples of coal were analysed, and their heats of combustion determined. The numbers actually obtained never agree with the values calculated from the composition or by means of Dulong or Cornut's equation. Usually the heat of combustion is greater than the sum of the heats of combustion of the constituents, but occasionally it is less. Cornut's formula gives the closest approximation to the real value. No explanation is yet possible of the difference between the real and calculated values. The important fact is that coal has been formed partly, at least, by endothermic reactions.

A coal from Gilly which contained 5 per cent. of oxygen gave a heat of combustion of 8553 Cal., whilst another coal from Sart-les-Moulins, containing only 1.5 per cent. of oxygen, developed only 8435 Cal. The heats of combustion of coals from the basin of North France vary between 8340 and 9257 Cal., the value usually lying between 8400 and 8800 Cal. It follows that these coals are somewhat richer than those of Saarbruck, which give numbers between 8215 and 8724. The highest results yet obtained were with two coals from Creuzot, namely, 9456 Cal. and 9623 Cal. C. H. B.

Expansion of Fluids and Change of Substance from the Fluid to the Gaseous State. By A. NADESCHIDIN (*Chem. Centr.*, 1888, 168, from *Rep. Phys.*, 23, 617—649, and 685—718).—The different theories which deduce one property of liquids from the others, attach special importance to the determination of the critical condition. In the present memoir the results of the determination of the critical pressure, the critical temperature, and the critical volume are given.

Scarcely any determinations of the critical volume have previously been made, but it is necessary to know it in order to precisely estimate the critical temperature and critical pressure; for only when the space which contains the liquids and vapours is equal to the critical volume, does the substance attain the critical condition. The critical volume is obtained when the liquid only changes its volume up to a point at which the limiting surface between the liquid and vapour disappears.

This was determined for a series of compounds by means of a series of small tubes, a fraction of whose volume was filled with the desired liquid. Those tubes were chosen in which when heated all the fluid volatilised, and in which too the disappearance and reappearance of the meniscus on cooling occurred in the middle, and not in proximity to the end of the tube. A series of theoretical and experimental researches have been made on the expansion of liquids at equal temperatures and at temperatures lying between wide limits.

J. P. L.

Determination of the Specific Weight and of the Vapour-pressure of Mixtures of Sulphurous and Carbonic Anhydrides. By A. BLÜMCKE (*Ann. Phys. Chem.* [2], 34, 10—21).—The experiments were carried out with apparatus of the same kind as that used by the author in his previous researches (*Abstr.*, 1885, 215; 1887, 435). The liquids used for comparison with carbonic anhydride were ether, benzene, and light petroleum, and for comparison with sulphurous anhydride, and with mixtures of the two, the author used mixtures of chloroform and ethylic alcohol. In his former researches, the values obtained for the specific weight of carbonic anhydride differed considerably at the higher temperatures from those given by Cailletet and Mathias (*J. de Phys.* [2], 5, 549). This he attributes to impurity in the carbonic anhydride used by him, and to his not having provided means of properly controlling the pressure at which the specific weight was determined, a defect which he has remedied in

the present research, and his results are now in close agreement with those obtained by these physicists.

The degree of concentration of the mixtures was not found to undergo alteration when the temperature was increased; for the author observed no sign of the escape of bubbles of carbonic anhydride, or of the formation of an emulsion, which latter was stated by Pictet (*Nouvelles machines frigorifiques*, 1885, 11) to occur when cooled below zero.

By a separate series of experiments, the author found that the percentage composition could be determined to a high degree of approximation from observations of the pressure.

The vapour-pressure was found to depend on the amount of fluid introduced into the apparatus, showing that the vapour was not saturated. This had previously been observed by Linde (*Allg. Hop. Brauerzeit.*, 1888, 299).

The specific weight was determined from the following interpolation formula:—

$$V(1 + n\alpha) = \frac{Vs + n\sigma}{S},$$

where p is the percentage by weight of carbonic anhydride in the mixture, n the number of volumes, at a pressure and temperature of 760 mm. and 0° respectively, of gaseous carbonic anhydride to an equal volume of liquid sulphurous anhydride, V the original volume of sulphurous anhydride, s its specific weight, $\sigma = 0.001965$, the specific weight of gaseous carbonic anhydride at 0° and 760 mm., S the specific weight of the mixture, and α a coefficient which, as in the case of mixtures of alcohol and carbonic anhydride, was not a constant, but increased with the value of p and with the temperature. With regard to the vapour-pressure, it was impossible for the author to compare his results numerically with those obtained by other experimenters, owing to the vapour being unsaturated, as in no case had the volume been determined. The principal question to be determined was therefore whether the vapour-pressure of sulphurous anhydride could at any temperature be diminished by the addition of carbonic anhydride, or whether its boiling point could be raised in the same manner.

According to Pictet (*Arch. Gen.*, **13**, 212) and Corsepius, the so-called Pictet fluid has a vapour-pressure, at temperatures above 30° , which is less than that of pure sulphurous acid, and, according to Grätz (*Allg. Brauer Hopfezeit.*, **17**, 1157) Turrettini and Rossi have obtained similar results. Rilliet obtains diametrically opposite results, and the author's observations confirm those of Rilliet. The author was unable to obtain any mixture with a higher boiling point than that of pure sulphurous anhydride, whilst Pictet, for example, gives -7.5° for the boiling point of the mixture CO_2S_7 , the author finds that at -17° it would have a pressure of 4 atmos.

G. W. T.

Internal Friction of Liquids. By L. GRAETZ (*Ann. Phys. Chem.* [2], **34**, 25—39).—The author observes that the large number of researches which have been made, from those of Poiseuille down-

wards, have not led to the determination of any definite relations between the internal friction of liquids and their chemical constitution. Graham was led to believe that such a relation must exist from the well-defined maximum values of internal friction in solutions of hydroxides.

With the object of finding such a relation, a large number of organic liquids were investigated by Graham himself (*Annalen*, **123**, 90), and also by Rellstab ("Transpiration homologer Flüssigkeiten," *Inaug. Diss.*, Bonn, 1868), Guerout (*Compt. rend.*, **81**, 1027), and Pribram and Handel (*Wien. Ber.*, **78**, 113; **80**, 1; **84**, 11), and a large number of saline solutions were experimented on by others. The results with the latter were practically *nil*, and those obtained with the former did not lead to the discovery of any definite relations, although the differences were found to be much greater than in gases, and the relations which appeared to hold in some cases were subject to numerous exceptions. The author formerly (*Ann. Phys. Chem.* [**2**], **25**, 340) came to the conclusion that the internal friction is not due mainly, as in gases, to molecular impacts, but to the direct action of molecular forces, he therefore considers only the residual internal friction after subtracting that of the substance in a gaseous state, the latter being due to molecular impacts.

Maxwell (*Phil. Mag.* [**4**], **35**, 129) showed that if μ is the coefficient of internal friction, E the modulus of rigidity, and T what he calls the *time of relaxation*, namely, the time during which a stress excited in the liquid falls to $1/e$ of its original value, then $\mu = ET$, independently of any hypotheses with regard to the nature of the internal friction. Starting with this equation, the author shows that to a first approximation, $\mu = A(\theta_0 - \theta)/\theta$, where θ is the temperature of the fluid, and θ_0 its critical temperature, both reckoned from that temperature for which μ becomes infinite. Calling this unknown temperature t_1 , the formula in centigrade degrees becomes

$$\mu = A(t_0 - t)/(t - t_1),$$

in which A and t_1 are unknown constants which have to be determined for each liquid.

The author made experiments on 61 different liquids, for which the critical temperature was either already known or could be determined, and in 54 of these he found that the observations were in close agreement with the formula. The seven exceptions consisted of ethylic ether and the six alcohols included in the liquids investigated. Those which agreed with the formula included various fatty acids, ethereal salts, haloid compounds of the fatty series, aldehydes, ketones, aromatic hydrocarbons, and water.

The author then calculated the values of a quantity $G = A/N$, where N is the number of molecules in unit volume of the liquid. The quantity G is a measure of the viscosity which is comparable for different liquids.

If n is the number of molecules per unit of length in the liquid (Hagenbach, *Ann. Phys. Chem.*, **109**, 358), the author gives the following table of the values of G for the normal acids and ethereal salts of these acids for values of n from 1 to 4.

	Acids.	Methyl salts.	Ethyl salts.	Normal propyl salts.	Normal butyl salts.	Isopropyl salts.	Isobutyl salts.
$n = 1$	747·7	—	942·3	1246·2	1725·2	1519·8	1593·0
$n = 2$	1039·0	1080·4	1246·8	1401·5	2034·5	1632·5	1802·2
$n = 3$	1320·5	1277·2	1539·2	1616·5	—	1993·6	2090·0
$n = 4$	1578·7	1506·5	1702·5	1780·0	—	2150·2	—

If each horizontal line be subtracted from the one above it, we get the following differences for each CH_2 -group in the acids—

	Acids.	Methyl salts.	Ethyl salts.	Normal propyl salts.	Normal butyl salts.	Isopropyl salts.	Isobutyl salts.
	291·3	—	304·5	155	309	236	209
	281·5	196·8	292·4	215	—	236	287
	258·2	229·3	163·3	164	—	156	—
Means	277·0	213·0	260·8	185	309	210	248

The differences of these mean values are not very great, and are within the limits of errors of observation. Similar relations are obtained in the case of organic chlorine and bromine compounds.

G. W. T.

Osmotic Pressure in the Analogy between Solutions and Gases. By J. H. VAN'T HOFF (*Zeit. physikal. Chem.*, 481—508).—The object of this paper is to establish an analogy which is supposed to exist between the state of substances in dilute solution and the same in the gaseous condition, and to show that osmotic pressure in the former is comparable with vapour-tension pressure in the latter case.

Suppose a solution contained in a vessel of semi-permeable material, that is to say, material permeable only by water molecules but not by the molecules of the dissolved substance, and that this vessel is immersed in water. Then, owing to the attraction of the molecules of the dissolved substance, water will enter the vessel, thus causing an increase of pressure, and this will continue until the pressure within the vessel is sufficient to counterbalance the attraction exercised by the molecules of the dissolved substance. Equilibrium being thus established, the pressure within the vessel is equal to the osmotic pressure, and may be taken as a measure of the same.

If we suppose the vessel to be fitted with a movable piston as a means of altering the pressure at will, it will then be possible to produce any alterations in the concentration and allow water to either enter or leave the vessel by decreasing or increasing the pressure. In this way a cycle of reversible changes may be performed, such as

decreasing the pressure and allowing water to enter, and then by restoring the pressure bringing the solution back to its original state, and the sum of the work done in such changes being zero, the second law of thermodynamics may be applied.

Vessels of such semi-permeable materials are the cells of plants, and observations with these have shown by the comparison of isotonic solutions (solutions of equal osmotic pressure) that the pressure is directly proportional to the concentration. Also if a porous cell, the walls of which have been thoroughly impregnated under pressure with copper sulphate solution to drive out the air, be filled with copper sulphate solution and then immersed in a solution of ferrocyanide, the two will by diffusion meet in the walls of the cell and there form a layer of copper ferrocyanide, which will act as a semi-permeable material to cane-sugar solution. Observations made by Pfeffer on cane-sugar solution with the aid of such a cell have shown that up to a 5 per cent. solution the pressure is directly proportional to the concentration. But this proportionality between pressure and concentration is precisely similar to Boyle's law in the case of gases, and if we consider the entrance of the water and subsequent increase of pressure to be in proportion to the number of molecules which come into contact with the walls of the cell in a given space of time, the argument is similar to that by which Boyle's law is looked on as due to molecular bombardment, and leads of course to the same conclusions.

By the aid of one of the reversible changes before mentioned, it may be shown that Gay-Lussac's law should also hold for solutions, and that osmotic pressure should be proportional to the absolute temperature. The experiments of Pfeffer with cane-sugar and sodium tartrate solution give numbers which are in satisfactory agreement with this law, as also the numbers obtained from observations of isotonic solutions. The observations of Soret, who kept two parts of the same solution at different temperatures and then determined the strength of each, also give numbers agreeing with the above.

It may be shown by means of reversible cycles that the osmotic pressure of a gas when in solution is equal to the tension of the same gas when in the free state. This of course leads directly to Avogadro's law in solution, so that for equal osmotic pressures and equal temperatures equal volumes of different solutions contain the same number of molecules, namely, that which is contained in the same volume of a gas under the same conditions of pressure and temperature. That this relation actually holds in practice is shown by a comparison of the osmotic pressures of a 1 per cent. sugar solution at different temperatures with the calculated tension of hydrogen gas containing the same number of molecules at the same temperatures.

If in the general expression for the relation of pressure, volume, and temperature in gases $PV = RT$, in accordance with Horstmann's suggestion, kilogram-molecules be always taken, the value of R becomes constant for all gases. The value of this constant is 845.05. The author points out that this number is in direct numerical relation with that which expresses in calories the value of a kilogram-metre, or the work equivalent $A = 1/423$. Hence $AR = 2$ approximately,

and the simple relation is obtained $APV = 2T$, a relation which may prove of value in future thermodynamical work.

From the theorem that solutions in the same solvent which have equal maximum vapour-tension or freezing point, must be isotonic, which is easily proved by the aid of a reversible cycle, Raoult's laws of the molecular reduction of vapour-tension and freezing point may be deduced, on the assumption that Avogadro's law holds good for solutions. The numbers thus calculated theoretically are in excellent agreement with those observed, and thus afford additional indirect support to Avogadro's law in solution. The molecular reduction of the freezing point t is found to be equal to $0.02 T^2/W$, where T is the freezing point in absolute temperature and W the latent heat of fusion of the solvent. In the case of ethylene bromide, the latent heat of fusion of which was unknown, the number calculated from the known molecular reduction of the freezing point was 13, and a subsequent determination by Pettersson gave as the observed value 12.94.

The marked exceptions which occur to Raoult's laws, especially in the case of electrolytes, find an explanation in the assumption first made by Arrhenius, that these latter in solution are partially dissociated into their ions. This must of course lead to a modification of Avogadro's law. This may be expressed in the general formula $APV = 2iT$, on the assumption that as dissociation of the molecules occurs these have i times their original numerical value, by the relation $APV = 2iT$. The value of i is easily calculated from Raoult's experiments, for since the molecular reduction of the freezing point in aqueous solutions of cane-sugar, which strictly obey Avogadro's law, is 18.5 and in this case $i = 1$, in other cases i will simply be the observed molecular reduction divided by 18.5.

A second method of calculating the value of i is given by Guldberg and Waage's theory, the application of which to the present case is shown in the paper. The agreement of the numbers thus obtained by different methods is a sufficiently satisfactory one, and therefore in its altered form Avogadro's law may be still said to hold good for dilute solutions.

H. C.

Chemical Equilibrium in Dilute Solutions. By M. PLANCK (*Ann. Phys. Chem.* [2], **34**, 139—154).—In a previous memoir (*Ann. Phys. Chem.* [2], **32**, 462), the author showed that the observed phenomena respecting the freezing and evaporation of dilute solutions could only be brought into accordance with the laws of thermodynamics by assuming that the molecules of the substance in solution undergo chemical decomposition to a greater or less extent, and found that van't Hoff's coefficient i (preceding Abstract) must be proportional to this chemical decomposition, or in other words must express the ratio of the actual number of molecules of the substance in solution to the number which there would be if no chemical decomposition took place. Arrhenius (*Zeit. physikal. Chem.*, **1**, 631) arrives at a similar conclusion, founded on the analogy between osmotic pressure in dilute solutions and the pressure of perfect gases. This analogy receives a good deal of support from chemical considerations inde-

pendently of purely theoretical ones, and the author thinks that it will probably be found to be in agreement with the theory derived from thermodynamical considerations; it will therefore be of interest to follow it into some of its consequences. The condition of equilibrium in a dilute solution must then be of the same character as the chemical equilibrium of various mutually reacting substances. The constituents of the molecules must themselves be considered as acting on each other, and not be treated as a mere mechanical mixture. If, for example, a dilute solution of hydrogen chloride, for which i is very nearly equal to 2, consisted of a mixture of free atoms of hydrogen and chlorine, these atoms could be either mixed or separated without expenditure of work, which is contrary to experience.

Let $\theta_0 - \theta$ be the lowering of the freezing point, $p_0 - p$ that of the pressure, θ_0 and p_0 being the temperature and pressure of the pure solvent, n_0 the number of molecules in the solvent, q_0 the heat of fusion of one of them, then, as the author has shown in the memoir previously referred to, n , the number of molecules of the substance in solution, is given by the equation—

$$n = \frac{n_0 q_0}{\theta_0^2} (\theta_0 - \theta) = n_0 \frac{p_0 - p}{p_0}.$$

Calling N the value which n would have if there were no chemical changes, n is generally greater than N for aqueous solutions, but is often less than N for benzene solutions. The value of i is n/N . Some of the molecules of the substance may enter into combination with molecules of the solvent, as occurs in the formation of hydrates, but as this does not alter the number of molecules in the solution, it cannot be determined from observations of the freezing point or of the pressure.

When a molecule can only break up in one way into two constituents, as is often the case for aqueous solutions, then if n_1 is the number of undecomposed molecules, and n_2 the number broken up into two constituents, $N = n_1 + n_2$, and $n = n_1 + 2n_2$, so that we have—

$$i = \frac{n}{N} = \frac{n_1 + 2n_2}{n_1 + n_2} = \frac{n_0}{N} \cdot \frac{q_0(\theta_0 - \theta)}{\theta_0^2} = \frac{n_0}{N} \cdot \frac{p_0 - p}{p_0},$$

n_1 and n_2 can therefore be uniquely determined in terms of N and i . The author confines himself to the consideration of solutions of this character. He finds that i depends on the temperature and the pressure, and also on the normal concentration N/n_0 .

Where K is a quantity depending on the pressure and temperature only, M is the normal molecular weight of the substance in solution, and $K/100M = k$, the author finds that the law connecting the molecular freezing point and lowering of vapour-pressure for dilute aqueous solutions is given by the equation—

$$i = 1 + \frac{\sqrt{1 + 2kP} - 1}{kP}.$$

Thence it is only in the limiting cases $k = \infty$ and $k = 0$ that the

ratio of the fall in the freezing point to the percentage strength of the solution is constant (Blagden's law), or the fall in the vapour-pressure in a constant ratio to the percentage strength (Wüllner's law), and in these cases there is either no dissociation or it is complete. Equations of a very similar character are obtained for other solvents.

Tamman's researches (*Mém. Acad. St. Pétersbourg* [7], 35, No. 9) on the vapour-pressure of aqueous solutions of various degrees of concentration, offer a means of testing the results obtained theoretically from the above equation. The results, however, do not agree with the theoretical ones, as in most of the experiments i increased with the concentration instead of diminishing. The author, however, points out that in the gases which are in a state of partial dissociation, it sometimes takes months before equilibrium is established: according to the analogy assumed to exist between gases and dilute solutions, a similar phenomenon may take place in the solutions, and this would seem to explain the discrepancies, although it would make it impossible to arrive at any definite results from measurements of the freezing point and vapour-pressure. Arrhenius, however, has shown (*loc. cit.*) that the value of i may be determined from the value of the electrical conductivity of the liquid, for if α is the coefficient of activity of the solution, that is, the ratio of the actual molecular conductivity to its value for an infinitely dilute solution, then for binary electrolytes, which are the only ones considered in the paper, $i = 1 + \alpha$. This gives a definite value for i , as the measurements of conductivity can be carried out very accurately, and are found to be in close agreement with each other. This leads to the inference that the establishment of chemical equilibrium in dilute solution is greatly facilitated by the passage through it of alternate currents, which calls to mind the assistance to the establishment of physical equilibrium rendered by mechanical disturbance.

The author finds that the conductivity, K , of a dilute solution is given by the equation—

$$K = \text{constant} \cdot (i - 1) P = a(\sqrt{1 + bP} - 1),$$

where P is the percentage (either by weight or volume, the equation being only a first approximation) of dissolved substance, and a and b are functions of the pressure and temperature only.

This formula agrees substantially with one given by Ostwald (*Zeit. physikal. Chem.*, 2, 36). It gives much better results than the ordinary quadratic interpolation formula, but the author finds that the theoretical formula obtained by proceeding to the second approximation, although too complicated to be convenient, gives results which are in close agreement with those obtained experimentally. Even this formula, however, gives no explanation of the existence of a maximum value of the conductivity, as is observed, for example, in the case of lithium chloride. The theory cannot, therefore, be applicable to concentrated solutions.

G. W. T.

Laws of Chemical Equilibrium. By H. LE CHATELIER (*Compt. rend.*, 106, 1008—1011).—A continuation of the discussion with Duhem.

Liebrich's Inactive Space. By R. GARTENMEISTER (*Annalen*, **245**, 230—235).—The author has repeated Liebrich's experiments on the existence of an inactive zone ("todten Raum") surrounding the space in which chemical reaction takes place in liquids. He finds that the hypothesis of this inactive zone is unnecessary, as the phenomena in question can be easily explained without its aid. For example, a test-tube is nearly filled with a mixture of sodium carbonate and chloral hydrate solution. It is then closed with a cork and inverted; after five minutes have elapsed the mixture becomes cloudy (owing to the formation of chloroform) except at the upper surface of the liquid. This remains clear, because the chloroform evaporates into the space above the surface of the liquid. When this space is saturated with chloroform vapour, then chloroform begins to separate out in the uppermost layers of the mixture. W. C. W.

Formation of Layers in Mixtures of Alcohol, Water, and Salts, or Bases. By J. TRAUBE and O. NEUBERG (*Zeit. physikal. Chem.*, **1**, 509—515).—Bodländer was the first to observe that on dissolving ammonium sulphate in mixtures of alcohol and water, at certain concentrations, the liquid divides into two well-defined layers. The authors find a similar behaviour with potassium and sodium hydroxides and carbonates, sodium phosphate and sulphate, zinc and magnesium sulphates, and other salts. They have therefore examined this change in the case of ammonium sulphate under varying conditions of temperature and concentration.

With a solution containing 340 grams of salt per litre, 750 c.c. of which is mixed with 250 c.c. of alcohol (99.6 per cent.), it is found that with increasing temperature there is in the upper layer a decrease in the relative amounts of water and salt, and an increase in that of the alcohol; in the lower layer, there is an increase of water, but a decrease of salt and alcohol. The change in the composition of the lower layer is, however, so small, that within tolerably wide limits of temperature it may be looked on as constant. Keeping the temperature constant, and increasing either the amount of alcohol or salt in solution, it is found that in the upper layer there is a decrease in the relative amounts of water and salt and an increase in that of the alcohol, in the lower layer there is a decrease in the alcohol and an increase in the salt, the water first increasing and then decreasing. In this way the addition of 40 grams of salt to a litre produce about the same effect as the addition of 100 grams of alcohol.

Experiments with potassium carbonate led to similar conclusions as those above quoted. It was not possible in either case to determine whether the components of the layers are present in definite molecular proportions, but this appears likely, especially in the case of the lower layer, the percentage composition of which has a great tendency to remain constant. H. C.

Absorption of Gases by Grey Vulcanised Caoutchouc. By G. HÜFNER (*Ann. Phys. Chem.* [2], **34**, 1—10).—As the result of a series of observations extending over a considerable period, the author arrives at the following conclusions.

Within the limits of temperature from 5° to 25° , no definite absorption coefficient of atmospheric air can be determined. An apparent absorption does take place, and during a series of experiments extending over six months this absorption was found to continue at a nearly uniform rate, but the author finds that it is due to a gradual disappearance of oxygen, caused probably by slow oxidation of the caoutchouc.

Within the temperature limits from 15° to 25° , there is no perceptible absorption of nitrogen. At a temperature of about -2° grey vulcanised caoutchouc absorbs about its own volume of dry carbonic anhydride. The specific coefficient of absorption of this gas diminishes with increasing temperature.

Within the limits of temperature from -2° to -13° , there was found to be no perceptible absorption of hydrogen, even after the caoutchouc had been in contact with the gas for three months.

G. W. T.

Inorganic Chemistry.

Methods for obtaining Constant Streams of Hydrogen Chloride, Ammonia, and Nitrogen. By G. NEUMANN (*J. pr. Chem.* [2], **37**, 342—345; compare Abstr., 1887, 769).—Hydrogen chloride can be generated in a Kipp's apparatus by the action of ordinary sulphuric acid on carnallite, and ammonia gas by allowing a solution of ammonia to react with solid potassium hydroxide. When the materials are exhausted, the solution of potash which is formed may be used for ordinary laboratory purposes after it has been boiled to expel ammonia.

To prepare nitrogen in a Kipp's apparatus, it is best to employ cubes containing chloride of lime made according to Winkler's method (Abstr., 1887, 442); these are treated with a mixture of equal volumes of ammonia and water. The resulting gas contains suspended ammonium chloride and other impurities, which may be removed by passing it through water, potash, and sulphuric acid.

The author describes an apparatus for obtaining constant supplies of these and other gases, which is superior to Kipp's, in that it is cheaper and that broken parts can be easily replaced. G. T. M.

Hyposulphates. By K. KLÜSS (*Chem. Centr.*, 1888, 215—216).—The following hyposulphates (dithionates) are described:—Bismuth, $\text{Bi}_2\text{O}_3, \text{S}_2\text{O}_5 + 5\text{H}_2\text{O}$; stannous, $8\text{SnO}, \text{S}_2\text{O}_5 + 9\text{H}_2\text{O}$; thorium, $\text{Th}(\text{S}_2\text{O}_6)_2 + 4\text{H}_2\text{O}$; normal and basic chromium salts, $\text{Cr}_2(\text{S}_2\text{O}_6)_3, 18\text{H}_2\text{O}$ and $3\text{Cr}_2\text{O}_3, 4\text{S}_2\text{O}_5 + 24\text{H}_2\text{O}$; uranium salts of the composition $7\text{UO}_2, \text{S}_2\text{O}_5 + 8\text{H}_2\text{O}$, $6\text{UO}_2, \text{S}_2\text{O}_5 + 10\text{H}_2\text{O}$, and $8\text{UO}_2, \text{S}_2\text{O}_5 + 21\text{H}_2\text{O}$; an ammonium salt, $(\text{NH}_4)_2, \text{S}_2\text{O}_5, \frac{1}{2}\text{H}_2\text{O}$; a beryllium salt, $5\text{BeO}, 2\text{S}_2\text{O}_5 + 14\text{H}_2\text{O}$; ferrous hyposulphate, $\text{FeS}_2\text{O}_5 + 7\text{H}_2\text{O}$, and the following basic ferric salts, $8\text{Fe}_2\text{O}_3, \text{S}_2\text{O}_5 + 14\text{H}_2\text{O}$, and $3\text{Fe}_2\text{O}_3, \text{S}_2\text{O}_5 + 8\text{H}_2\text{O}$. The normal ferric

salt is unstable in the solid state. Normal copper hyposulphate, $\text{CuS}_2\text{O}_6 + 5\text{H}_2\text{O}$, and several basic salts, $4\text{CuO}, \text{S}_2\text{O}_5 + 3$ and $4\text{H}_2\text{O}$, a mercury salt, $5\text{HgO}, 2\text{S}_2\text{O}_5$, and an aluminium salt, $\text{Al}_2\text{O}_3, 3\text{S}_2\text{O}_5 + 18\text{H}_2\text{O}$, were also prepared. Attempts to prepare hyposulphate of zirconium and vanadium failed. Hyposulphuric acid is without effect on cerium dihydroxide and thallium hydroxide at the ordinary temperature; on heating, the acid decomposes with evolution of sulphur dioxide, which reduces the hydroxide.

In the second part of the paper, the author discusses the isomorphism of the hyposulphates, and describes the preparation of different double salts. Double salts of ammonium hyposulphate with hyposulphates of magnesium, zinc, cadmium, ferrous oxide; manganous oxide, nickel, cobalt, aluminium, and copper are described. The following isomorphous mixtures were analysed: barium with lithium and silver salts, and thallium with sodium, lithium, silver, and barium salts. There does not appear always to be such a sharply defined line between double salts and an isomorphous mixture as has hitherto been supposed.

J. P. L.

Nitrous Anhydride and Nitrosyl Chloride. By A. GEUTHER (*Annalen*, **245**, 97—99).—The mixture of nitrogen sesquioxide and peroxide obtained by the action of nitric acid (sp. gr. 1.4) on arsenious oxide, may easily be separated by distillation, if the vapours are first passed into a flask at 30° before entering the receiver, which is surrounded by ice and salt. The sesquioxide boils at 35° . Its specific gravity has been determined at different temperatures—

-8°	1.464	}	0°	1.449
-4	1.4555		$+1$	1.4485
-1	1.451		$+2$	1.447

The peroxide boils at 26° . Its specific gravity varies from 1.5035 at -5° to 1.4935 at 0° , and 1.474 at 15° .

The specific gravity of nitrosyl chloride is—

At -18°	1.433
-15	1.425
-12	1.4165

Nitryl chloride does not appear to exist.

W. C. W.

Action of Carbon Tetrachloride on Inorganic Oxygen Compounds free from Hydrogen. By H. QUANTIN (*Compt. rend.*, **106**, 1074—1076).—The various oxygen compounds were heated at different temperatures in the vapour of the tetrachloride.

Barium and sodium carbonates at dull redness are completely converted into chlorides with evolution of carbonic anhydride and carbon oxychloride. Geuther obtained a mixture of carbonate and chloride by the action of the tetrachloride on the oxides of these metals, but probably the chloride which was formed melted and protected the carbonate from the action of the vapour.

Carbonic anhydride, boric anhydride, and silicic anhydride offer

similar resistances to the reducing action of carbon tetrachloride, and hence it was of interest to compare the behaviour of carbonates, borates, and silicates. Ferric and aluminium borates are completely volatilised at a red heat, the boric acid being partially converted into boron trichloride and partially volatilised as the anhydride. Kaolin is distinctly attacked under the same conditions. Silicates rich in silica yield a small quantity of silicon tetrachloride, the amount increasing with the proportion of alumina in the silicate.

Barium and potassium sulphates at a red heat are partially converted into chlorides, with formation of pyrosulphuryl chloride, carbonic anhydride, and carbon oxychloride.

Calcium phosphate at a red heat yields calcium chloride and phosphorus pentachloride. By the action of chlorine and carbonic oxide on the phosphate at a lower temperature, Riban obtained phosphorus oxychloride. It follows that the interaction of carbon tetrachloride and phosphorus oxychloride at a red heat yields phosphorus pentachloride.

Tungstic anhydride at dull redness yields the oxychlorides WOCl_2 and WOCl_4 , whilst molybdic and uranic anhydrides yield mixtures of chloride and oxychloride.

From these results it follows that oxygen compounds which contain no hydrogen are attacked by carbon tetrachloride at a high temperature, the metal and the non-metal being converted into oxychloride, if the latter can exist in presence of excess of carbon tetrachloride. The tetrachloride is converted into carbonic anhydride and carbon oxychloride. If the temperature is so high that the oxychlorides are reduced by the excess of the tetrachloride, metallic and non-metallic chlorides only are obtained.

C. H. B.

Sodium Potassium Carbonate. By L. HUGOUNENQ and J. MOREL (*Compt. rend.*, **106**, 1158—1160).—A solution containing per litre 495.9 grams of potassium iodide, 10.3 grams of potassium carbonate, 77.3 grams of sodium carbonate, 42.0 grams of disodium phosphate, and 58.3 grams of sodium chloride, when allowed to evaporate spontaneously, yields large, transparent, prismatic crystals containing the two carbonates together with water of crystallisation. They are slightly efflorescent, begin to melt at about -40° , and dissolve in their own weight of water. The crystals are monoclinic prisms, the dominant face being *me*¹, and the ratios of the axes $a : b : c = 0.7104 : 1.0 : 0.78$, with an inclination of $75^\circ 35'$. When dissolved in water and recrystallised, the crystals have not the same composition, but contain a higher proportion of potassium, and approximate more closely to Margueritte's salt, $\text{K}_2\text{CO}_3 \cdot 6\text{H}_2\text{O} + 2(\text{Na}_2\text{CO}_3 \cdot 6\text{H}_2\text{O})$. The composition of the original crystals agrees fairly well with the formula $\text{K}_2\text{CO}_3 \cdot 6\text{H}_2\text{O} + 3(\text{Na}_2\text{CO}_3 \cdot 6\text{H}_2\text{O})$, but only when they have been formed under the particular conditions described above. There can be little doubt that the crystals are not true double salts, but mixtures of isomorphous salts.

C. H. B.

Compound of Zinc Oxide with Sodium Hydroxide. By A. M. COMEY and C. L. JACKSON (*Ber.*, **21**, 1589—1590).—When a solu-

tion of zinc or zinc oxide in strong aqueous soda is shaken with alcohol, the liquid separates into two layers. The lower, aqueous, layer is again treated two or three times with alcohol, when it solidifies to a crystalline mass. The alcoholic solution, under circumstances not yet determined, deposits lustrous needles in conical or spherical groups. The crystals have the composition expressed by the formula $2\text{NaOZnOH} + 7\text{H}_2\text{O}$. They do not melt at 300° , and are decomposed by alcohol, and by water when free alkali is not present. The composition of the crystals first mentioned was not determined, but they seem to differ from the other crystals only in having a larger amount of water of crystallisation; they melt below 100° .

N. H. M.

Action of Sodium Thiosulphate on Cupric Salts. By G. VORFMANN (*Monatsh.*, 9, 165—179).—The compound obtained when a solution of sodium thiosulphate is added to a solution of copper sulphate has been investigated by many experimenters, and various formulæ have been assigned to it. The author's results are as follows. A greenish-yellow salt, $\text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$, separates in the form of microscopic prisms when saturated solutions of copper sulphate and sodium thiosulphate in the proportion of 1 mol. of copper sulphate to 2 mols. of sodium thiosulphate are mixed and allowed to stand at the ordinary temperature. Sodium tetrathionate is also formed. When, however, the solutions are previously heated to 40° and then mixed, the temperature rises $5\text{--}7^\circ$, and on standing in water at 40° an intensely citron-yellow salt, $3\text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3 + 8\text{H}_2\text{O}$, separates in the form of microscopic prisms. When this salt is washed with alcohol and dried over sulphuric acid, it loses 3 mols. H_2O , but if left too long it gradually decomposes. This citron-yellow salt can also be prepared from the greenish-yellow one by continued washing with cold water, and it is always formed when the solutions of copper sulphate and sodium thiosulphate are warm or dilute. It is unstable, decomposes, and becomes black on standing. When boiled with water or dilute sulphuric acid, it is decomposed: $3\text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3 \cdot 8\text{H}_2\text{O} = 3\text{Cu}_2\text{S} + 2\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + \text{S}_2 + 2\text{SO}_2 + 7\text{H}_2\text{O}$.

Attempts to prepare copper thiosulphate were unsuccessful.

Salts containing more than 1 mol. of sodium thiosulphate to 1 mol. of copper thiosulphate, such as $\text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3 + 4\text{H}_2\text{O}$; $\text{Cu}_2\text{S}_2\text{O}_3 \cdot 3\text{Na}_2\text{S}_2\text{O}_3 + 2\text{H}_2\text{O}$, and $\text{Cu}_2\text{S}_2\text{O}_3 \cdot 4\text{Na}_2\text{S}_2\text{O}_3 + 6\text{H}_2\text{O}$, are best obtained by mixing a solution of the citron-yellow salt with a solution of the calculated quantity of sodium thiosulphate and adding alcohol. The double salts separate as oily liquids which solidify when treated with fresh quantities of absolute alcohol. They are yellow to white, crystalline compounds, which are more stable and less readily decomposed when boiled with water than the salts described above. They do not decompose on keeping, and are readily soluble in water, but are not deliquescent. With barium salts, their aqueous solutions give a white precipitate, $\text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{BaS}_2\text{O}_3 + 7\text{H}_2\text{O}$, which is soluble in hydrochloric acid, but almost insoluble in water.

F. S. K.

Vapour-density of Aluminium Chloride and the Valency of the Elements of the Aluminium Group. By L. F. NILSON and O. PETTERSSON (*Zeit. physikal. Chem.*, **1**, 459—464).—Aluminium chloride, when heated in an atmosphere of carbonic anhydride, gives at a temperature a little below 835° , a vapour-density agreeing with the formula AlCl_3 , without any sign of decomposition. If heated above 935° , the chloride begins to attack the platinum vessel.

Since for indium chloride the formula InCl_3 has been established, there can be little doubt of the trivalency of the aluminium metals. It is extremely probable that in accordance with this view, gallium chloride has the formula GaCl_3 , which, indeed, Friedel's experiments seem to indicate. H. C.

Passivity of Iron and Nickel. By E. SAINT-EDME (*Compt. rend.*, **106**, 1079—1080).—Commercial sheet nickel is passive in ordinary nitric acid, whereas iron is only passive in the fuming acid; but iron in contact with nickel becomes passive in the ordinary acid. Iron becomes passive gradually, but nickel is passive immediately. If iron and nickel are introduced into the acid together, the iron likewise becomes passive instantly. Electrolytic nickel from an ammoniacal solution of the chloride or sulphate is passive immediately.

Iron is only passive when azotised, and loses its passivity if heated in hydrogen. Passive nickel when heated to bright redness in a current of pure hydrogen yields a small quantity of ammonia and acquires a silvery lustre, but remains passive, and hence it would seem that the nickel retains some of the nitrogen very tenaciously.

C. H. B.

Nickel Ammonium Oxalate. By K. KRAUT (*Annalen*, **245**, 239—240).—Nickel oxalate dissolves in ammonia, and the solution deposits green, microscopic crystals of the composition $2\text{NH}_3 \cdot \text{NiC}_2\text{O}_4 + 5\text{H}_2\text{O}$. The compound effloresces on exposure to the air and loses 3 mols. H_2O . W. C. W.

Phosphotungstic and Arsenotungstic Acids. By F. KEHRMANN (*Annalen*, **245**, 45—57).—The derivatives of phosphotungstic acid have been previously described by the author (*Abstr.*, 1887, 777). The arsenotungstic acid which Fremery obtained by adding dilute sulphuric acid to barium tungstate suspended in a solution of arsenic acid, is not a homogeneous compound, but consists of a mixture of two acids. The separation of the acids is accomplished by the method used for the separation of the phosphotungstic acids (*loc. cit.*).

α -Arsenoluteotungstic acid, $\text{AsH}_3\text{W}_8\text{O}_{28} + 16\text{H}_2\text{O}$, is analogous to the phospholuteotungstic acid, and the salts of the two acids are isomorphous. The potassium salt, $\text{K}_3\text{AsW}_8\text{O}_{28} + 8\text{H}_2\text{O}$, is triclinic. The acid is very stable; the arsenic acid is not reduced by sulphuretted hydrogen. W. C. W.

Titanium. By T. KOENIG and O. v. D. PFORDTEN (*Ber.*, **21**, 1708—1716).—Titanic acid trichloride, $\text{TiCl}_3 \cdot \text{OH}$, is readily obtained by mixing the theoretical quantities of titanium chloride and 36 per cent. hydrochloric acid, the reaction being extremely energetic. It is

a yellow, spongy, very deliquescent mass which dissolves very readily in water and alcohol with a hissing noise; it also dissolves in ether with a similar energetic reaction, but when more ether is added, a white, deliquescent compound is precipitated. An aqueous solution is tolerably stable, but titanous acid is precipitated after continued boiling. When heated in the dry state, it is decomposed into titanous acid and titanous chloride; the same decomposition takes place when it is heated in a current of hydrogen or hydrogen chloride.

Titanous acid dichloride, $\text{Ti}(\text{OH})_2\text{Cl}_2$, is prepared by adding titanium chloride to a slight excess of hydrochloric acid; by the action of titanium chloride on the calculated quantity of 36 per cent. hydrochloric acid; or by adding titanium chloride to the requisite quantity of well-cooled water. It is a very voluminous, yellow, exceedingly deliquescent mass or a vitreous solid, according to the method of preparation. It is soluble in alcohol and ether, but a white compound is precipitated when an ethereal solution is strongly diluted with absolute ether. Titanous acid separates when an aqueous solution is boiled. When heated in the dry state, it is rapidly decomposed, yielding titanous acid and hydrogen chloride.

Titanous acid monochloride, $\text{Ti}(\text{OH})_3\text{Cl}$, is formed when the dichloride or trichloride is allowed to remain for some time exposed to the air at the ordinary temperature. Both compounds deliquesce, with evolution of hydrogen chloride, but at the end of about a month's time they solidify. The product contains, approximately, 2 mols. H_2O after remaining for two months over sulphuric acid. When placed in a desiccator containing phosphoric anhydride, it loses 1 mol. H_2O in 14 days, and after a long time the anhydrous compound is obtained. In one experiment it was obtained in a crystalline form. It is a white compound which is stable in the air, and far less readily soluble in water than the dichloride or trichloride. In order to obtain a clear aqueous solution of the anhydrous compound, a few drops of hydrogen chloride must be added; titanous acid is precipitated from this solution on boiling. It is insoluble in alcohol and ether. When heated, it yields titanous acid, hydrogen chloride, and water. F. S. K.

Titanium Trioxide. By A. PICINI (*Ber.*, **21**, 1391—1393), and by A. CLASSEN (*Ber.*, **21**, 1519).—A question of priority.

Thio-derivatives of Antimonic Acid. By W. FEIT and K. KUBIERSCHKY (*Ber.*, **21**, 1660—1662).—Attempts were made to prepare thio-derivatives of antimonic acid:—(1.) By adding antimony pentasulphide to strong aqueous soda until a portion remained unacted on; on adding alcohol to the solution, sodium tetrathioantimonate separated in well-formed tetrahedra, no other compound being formed. (2.) By adding antimony sulphotrichloride to aqueous soda. (3.) By the action of lead oxide on sodium tetrathioantimonate. (4.) By the action of antimony oxytrichloride on sodium sulphide. (5.) By boiling a solution of sodium metantimonate with sodium sulphide. In (2) and (4) the tetrathioantimonate was formed. The author concludes that thio-derivatives of antimonic acid containing less than 4 atoms of sulphur cannot exist. N. H. M.

The Anomalous Density of Liquid Bismuth. By C. LÜDEKING (*Ann. Phys. Chem.* [2], **34**, 21).—The author finds that, like water, liquid bismuth attains a maximum density just before becoming solid. The expansion from the point of maximum density the author finds from the mean of two determinations to be 0.0000864, and the expansion at the moment of solidification to be about 3 per cent. of the volume, or about a third of that of water. Vincentini (*Atti R. Acc. Sc. Torino*, **22**, 23) gives a value three times as great for the instantaneous expansion, and was unable to find any expansion before solidification. He however used a dilatometer much less delicate than that employed by the present author, and the latter ascribes the high value obtained by Vincentini for the expansion on solidifying, to the presence of air in his dilatometer, as he considers that this could not be avoided in the method used by him. G. W. T.

Sodium Platosammonium Sulphite. By W. HABERLAND and G. HANEKOP (*Annalen*, **245**, 235—238).—When a solution of chloroplatinic acid is saturated with sulphur dioxide and the liquid neutralised with sodium carbonate, a white precipitate is thrown down which is soluble in hydrochloric acid. On the addition of ammonia in excess to the acid solution, rhombic crystals of sodium platosammonium sulphite, $2\text{NH}_3\cdot\text{Pt}(\text{SO}_3\text{Na})_2 + 5\frac{1}{2}\text{H}_2\text{O}$, are slowly deposited. This salt is analogous to the ammonium salt described by Peyrone (*Gmelin-Kraut's Handbuch*, **3**, 1099). W. C. W.

Rhodium Sesquichloride. By E. LEIDIÉ (*Compt. rend.*, **106**, 1076—1079).—When rhodium is heated in chlorine to incipient redness, the lowest temperature at which the action proceeds readily, the proportion of chlorine in the product never approaches that existing in the sesquichloride, and is less the higher the temperature. With a rapid current of chlorine at bright redness, a deposit with the colour of peach-blossom forms on the cold part of the tube, but it is a product of dissociation, and its composition is variable. At 350° or 440°, chlorine attacks rhodium very slowly.

Fellemborg's method of heating rhodium sulphide in chlorine yields no definite results, and a temperature sufficient to secure the complete expulsion of the sulphur decomposes the chloride. The action of sulphuric acid on the rhodichlorides yields rhodium sulphate, and not, as Claus states, rhodium chloride.

Hydrated rhodium sesquichloride, or hydrated ammonium rhodichloride, when heated in pure and dry nitrogen at 440°, yields only rhodium sesquioxide, hydrogen chloride, or hydrogen chloride and ammonium chloride being evolved.

The best method of obtaining anhydrous rhodium sesquichloride is to heat the alloy, RhSn_3 , described by Debray (*Abstr.*, 1887, 779), in a current of chlorine at 440°, a temperature at which the chloride does not dissociate. Stannous chloride volatilises. The product is allowed to cool completely in a current of chlorine, and this gas is then displaced by carbonic anhydride. Rhodium sesquichloride thus obtained is a brick-red powder, which retains the crystalline form of

the alloy. The results of the analyses agree exactly with the formula Rh_2Cl_6 .

The author has prepared and examined a number of rhodiochlorides.

Ammonium rhodiochloride, $\text{Rh}_2\text{Cl}_6, 6\text{NH}_4\text{Cl} + 3\text{H}_2\text{O}$, has the crystalline form described by Keferstein. The author was unable to obtain the chloride, $\text{Rh}_2\text{Cl}_6, 4\text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$, described by both Vanquelin and Claus, who, however, differ considerably in their description. The sodium salt has the composition $\text{Rh}_2\text{Cl}_6, 6\text{NaCl} + 18\text{H}_2\text{O}$. The potassium salt, $\text{Rh}_2\text{Cl}_6, 4\text{KCl}$, crystallises in the rhombic system as stated by Berzelius, but it contains no water. The hydrated chloride, $\text{Rh}_2\text{Cl}_6, 6\text{KCl} + 6\text{H}_2\text{O}$, described by Claus, could not be obtained.

C. H. B.

Mineralogical Chemistry.

Phosphorescent Blende. By A. VERNEUIL (*Compt. rend.*, 106, 1104—1107).—Natural hexagonal crystals of blende have comparatively feeble phosphorescent properties. If natural zinc sulphide is distilled in a slow current of hydrogen some hydrogen sulphide is evolved, and small hexagonal crystals of zinc sulphide are obtained, which show a brilliant green phosphorescence. The same result is obtained by distilling artificial zinc sulphide, but non-phosphorescent hexagonal crystals are also obtained. The crystals which form in the front part of the tube always show the most brilliant phosphorescence.

The phosphorescence is not due to impurities in the hydrogen, nor yet to impurities derived from the tube, since the same results are obtained if the zinc sulphide is heated in a platinum boat. Variations of temperature between an orange-red heat and a full white heat are without influence, and variations in the velocity of the current of hydrogen likewise have no material effect.

If zinc sulphide is heated in a platinum dish in a stationary atmosphere of hydrogen, hydrogen sulphide is evolved and some metallic zinc is obtained, and the product is not phosphorescent. With a moderately rapid current of gas, the phosphorescence appears, and with a rapid current the same results are obtained as when the zinc sulphide is in contact with the sides of the tube.

C. H. B.

Analyses of Franklinite. By G. C. STONE (*Zeit. Kryst. Min.*, 14, 291—292, from *School of Mines Quarterly*, 8, 148—152).—The author has analysed a series of specimens picked from ore from the two mines of the New Jersey Zinc and Iron Company, in Sussex Co., New Jersey. The ore from the Sterling Hill Mine, near Ogdensburg, is mostly franklinite with calcite and some zincite, whilst that

from the Taylor mine at Franklin Furnace is mainly franklinite, willemite, and zincite. Analysis gave the following results:—

	Ia.	Ib.	IIa.	IIb.	IIc.	IIId.
Fe ₂ O ₃	0·44	0·36	67·38	66·34	60·52	56·57
Mn ₂ O ₃ . . .	—	—	—	—	6·79	10·52
MnO	6·50	5·54	16·38	12·31	12·81	16·37
ZnO	93·28	94·30	16·28	20·26	19·44	15·91
Totals	100·22	100·20	100·04	98·91	99·56	99·37
Sp. gr.	5·53	5·51	5·21	5·07	5·19	5·14

I. Zincite, *a*, dark-red grains; *b*, dark-red round lamellar mass.
 II. Franklinite. Of this mineral, the author finds two distinct varieties, both corresponding with the general formula RO, R₂O₃. One variety (IIa and *b* from Sterling Hill) has a dull lustre, and dissolves with difficulty in hydrochloric acid without any evolution of chlorine, whilst the other (IIc and *d* from Taylor mine) has more lustre, and dissolves very readily in hydrochloric acid with evolution of chlorine. The following are analyses of willemite from the Taylor mine: *a*, nearly white, dull; *b*, pale-green, vitreous; *c*, orange, dull; *d*, greenish-yellow to bright-yellow, vitreous; *e*, dark-red, dull.

	IIIa.	IIIb.	IIIc.	IIId.	IIIe.
SiO ₂	27·20	26·92	28·30	27·48	27·14
ZnO	65·82	65·04	66·68	63·88	64·38
MnO	6·97	7·78	4·92	8·33	6·30
FeO	0·23	0·51	0·31	0·49	1·24
Totals	100·22	100·25	100·21	100·18	99·06
Sp. gr.	4·19	4·19	4·18	4·16	4·13

Tephroite gave the following results:—

SiO ₂ .	MnO.	ZnO.	FeO.	MgO.	Total.
30·63	49·80	5·74	3·33	10·16	99·66

B. H. B.

Pseudomorph of Manganite: Artificial Formation of Pyrolusite. By A. GORGEU (*Compt. rend.*, 106, 1101—1104).—When manganite, Mn₂O₃.H₂O, is heated for about seven hours at 270—310°, in presence of air, it is completely converted into the peroxide. With the crystallised mineral, the change requires a longer time. The crystals retain their metallic lustre, but the colour changes from violet to iron-grey. The hardness 3·0 is sensibly equal to that of pyrolusite, and a similar agreement is observed between the specific gravities. Direct measurements show that the crystals retain their original form. It follows that under the conditions described,

polianite is obtained as a pseudomorph after manganite. In other words, manganese peroxide has been prepared artificially with a form and properties common in the natural mineral.

Direct experiment shows that the conversion of manganite into the peroxide by heating in contact with air is practicable on a large scale, with a corresponding increase in the oxidising value. The mineral must be heated gradually, so that the water is expelled slowly, otherwise the absorption of oxygen is comparatively small. Braunite, hausmannite, and psilomelane do not absorb oxygen in notable quantity between 200° and 425°. Manganous carbonate under these conditions oxidises slowly and incompletely.

C. H. B.

Lansfordite, a New Mineral. By F. A. GENTH (*Zeit. Kryst. Min.*, 14, 255—256).—This interesting mineral was found, in small stalactites, in a fissure in the roof of a gallery in the Lansford anthracite mine, near Tamaqua, in Schuylkill Co., Pennsylvania. The stalactites are white and transparent, and exhibit crystalline structure. Their hardness is 2·5, and their sp. gr. 1·692. Analysis gave results corresponding with the formula $3\text{MgCO}_3, \text{Mg}(\text{OH})_2 + 21\text{H}_2\text{O}$.

B. H. B.

Occurrence of Thenardite in Russia. By W. MARKOWNIKOFF (*J. Russ. Chem. Soc.*, 1887, 245—252).—It is known that in the bitter lakes of South Eastern Russia (on the north of the Caspian Sea, and east of the mouth of the Volga) sodium sulphate occurs in solution, and in 1884 the author showed that the principal constituent is astrachanite; he has now ascertained that anhydrous sodium sulphate, thenardite, also occurs in a nearly pure state, being formed in the lakes under the influence of the high summer temperature. The author finds that the quantity of magnesium (and of astrachanite) in the salts (A) is greater near the delta of the Volga, and less (B) as we proceed in an easterly direction; this is shown by the following analyses:—

	Na_2SO_4 .	MgSO_4 .	CaSO_4 .	NaCl .	Insoluble residue.	H_2O .	Total.
(A.)	74·95	3·97	1·44	2·62	0·89	17·00	99·88
(B.)	96·31	0·69	0·22	2·31	0·29	0·10	99·92

Thenardite is also found in the Caucasus; this, however, is not of recent date, like that from the Astrachan lakes, but belongs to a former geological epoch. A sample was analysed by the author:—

Na_2SO_4 .	CaSO_4 .	H_2O .	Total.
99·69	0·28	0·15	100·12 per cent.

Thenardite is also found in the Kirgisian mountain, Tchaptchali, between rock salt layers, in the permian formation. The author thinks that the occurrence of thenardite in the said lakes is due to the contact of water with these layers, as the mother-liquor from which thenardite is deposited, according to his analyses, does not

contain a sufficient quantity of magnesium salt to warrant the assumption that it has been formed by double decomposition from magnesium sulphate and sodium chloride. B. B.

Dihydrothenardite, a New Mineral. By W. MARKOWNIKOFF (*J. Russ. Chem. Soc.*, 1887, 252—254).—This salt, $\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$, has been found in the Lake Gori, of the Tiflis Government. It is found on the shore as a layer, 1 cm. in thickness, and is even in outward appearance different from astrachanite, thenardite, and mirabilite. Its structure appears to be crystalline, the fracture is colourless, but the surface is opaque from slight efflorescence, which, however, does not go on very quickly. Its analysis gave the following result:—

Water at 250°.	Na_2SO_4 .	NaCl .	Total.
16.15	81.18	0.98	98.32

The difference from 100° is due to traces of clay, gypsum, and magnesium sulphate. The crystalline form was determined by G. N. Wyruboff, of Paris, who in vain tried to obtain this new hydrate artificially. In the purest sample, 19.6 per cent. of water was found (instead of 20.2 as required by theory). The crystals are monoclinic; $a : b : c = 0.4651 : 1 : 0.7194$; $\gamma = 101^\circ 5'$. It is probable that salt A quoted in the preceding paper consists chiefly of dihydrothenardite. B. B.

Pharmacolite. By H. DUFET (*Compt. rend.*, 106, 1238—1240).—A vessel containing a solution of disodium arsenate was placed inside a vessel containing a solution of calcium nitrate, water was added, and the two salts were allowed to mix by diffusion. Under these conditions well-defined, monoclinic prisms of pharmacolite are obtained, identical in form with the crystals described by Haidinger and Schrauf. They have the composition $\text{CaHAsO}_4 + 2\text{H}_2\text{O}$, not $2\text{CaHAsO}_4 + 5\text{H}_2\text{O}$, as stated by Klaproth and by Rammelsberg, and they are isomorphous with brushite, $\text{CaHPO}_4 + 2\text{H}_2\text{O}$. Details of the measurements of the crystals are given. C. H. B.

A Crystallised Slag. By F. FOUQUÉ (*Zeit. Kryst. Min.*, 14, 283—284, from *Bull. soc. fran. min.*, 9, 287).—A slag from the St. Nazaire Works contained a crystallised substance, whose form was cubic, whilst its optical properties were partly those of a positive uniaxial crystal and partly anomalous. Its hardness was less than 5, and its sp.gr. 2.91. Analysis gave the following results:—

SiO_2 .	Al_2O_3 .	CaO .	MgO .	Fe_2O_3 .	Total.
37.60	12.26	40.11	9.33	trace	99.30

This composition is nearly that of melilite, which, however, contains less silica, and has a negative double refraction. It also invariably contains ferric oxide and alkalis. B. H. B.

Spodumene from Brazil. By P. JANNASCH (*Jahrb. f. Min.*, 1888, i, Mem., 196—201).—The author has made a very careful analysis of transparent, yellowish-green spodumene from Brazil, the results being as follows:—

SiO ₂ .	Al ₂ O ₃ .	FeO.	MnO.	CaO.	Li ₂ O.	Na ₂ O.	H ₂ O.	Total.
64·32	27·79	0·67	trace	0·17	7·45	0·55	0·12	101·07

The sp. gr. is 3·174. These analytical results are in accord with Doelter's formula for spodumene, Li(Na)₂Al₂Si₄O₁₂. Compared with recent analyses of spodumene, this analysis shows the highest percentage of lithia and the lowest of soda.

B. H. B.

Products of the Alteration of Rhodonite. By A. H. CHESTER (*Jahrb. f. Min.*, 1888, i, Mem., 187—190).—A specimen of manganese ore, resembling v. Kobell's klipsteinite, was found by the author to be an altered rhodonite. The results of the analysis of the portion soluble in hydrochloric acid (Ib) and of the insoluble portion (Ia) are given. The substance is undoubtedly a mixture of two minerals, the soluble one being formed by the combination of the other with oxygen and water.

	Ia.	Ib.	IIa.	IIb.	III.
SiO ₂	26·22	—	43·31	0·23	48·75
MnO	15·54	—	15·49	—	30·66
FeO	6·44	—	8·44	—	10·85
CaO	0·75	0·90	2·20	1·82	6·21
MgO	—	4·24	11·74	4·89	0·91
Mn ₂ O ₃	—	30·07	—	4·74	—
Fe ₂ O ₃ + Al ₂ O ₃	—	7·95	—	4·65	—
CO ₂	—	—	—	—	1·70
H ₂ O	—	7·94	—	2·25	0·80
Total	—	100·05	—	99·76	99·88

The analysis shows that the insoluble portion consists of rhodonite in which FeO is substituted for a portion of the MnO, and that the soluble portion is wad. The mineral is therefore merely a mixture of these two.

A mineral from Cumberland, Rhode Island, known as marceline, was analysed in the same way. The insoluble portion (IIa) is rhodonite, in which MnO is largely replaced by FeO and MgO. The soluble portion (IIb) is wad containing a large portion of lime and magnesia.

A specimen of so-called photicite (Analysis III) from Cumberland, Rhode Island, is obviously nothing more than a slightly altered rhodonite. None of these three minerals therefore deserves a special name; they should all be classed as more or less altered rhodonite.

B. H. B.

Clay Slate and Sericite Slate. By A. v. GRODDECK (*Jahrb. f. Min.*, 1888, i, Ref., 415—417; from *Jahrb. k. preuss. geol. Landes-anst. fur 1885*, 1—52).—The author gives 17 analyses of clay slates from the

Upper Harz. The microscopical examination showed that the Culm clay slate and the Devonian clay slate contained quartz, a sericite-mica, and a chloritic mineral as principal constituents. Carbonaceous matter, carbonates, and needles of rutile were also observed. Black vein-clay (the soft clay lying between the ore and the sides of the vein) exhibits as a rule the same mineralogical constitution. The coloured vein-clays consist only of quartz and sericite, needles of rutile, and a quantity of iron ore (goethite?). The alteration of clay state to vein-clay seems to be due to a decrease of the chloritic constituents, which in the former average 16.54 per cent., and fall to 4.37 per cent. in the black vein-clay and to zero in the coloured variety. B. H. B.

Analysis of Roncegno Water. By M. GLÄSER and W. KALMANN (*Ber.*, 21, 1637—1639).—The water from Roncegno (South Tyrol) is yellow from the presence of ferric sulphate. The following numbers which show the weight in grams per litre of water at 18° of the several constituents form the mean of two series of analyses:—

SiO ₂ .	SO ₃ .	As ₂ O ₅ .	P ₂ O ₅ .	Cl.	CuO.	FeO.
0.1283	4.4675	0.1621	0.0123	0.0027	0.0037	0.0303
Fe ₂ O ₃ .	MnO.	CoO.	NiO.	Al ₂ O ₃ .	CaO.	
1.2495	0.1087	0.0114	0.0381	0.4343	0.7821	
MgO.	K ₂ O.	Na ₂ O.	Organic matter.			
0.1210	0.0163	0.1270	0.2246			

Total solids = 7.9396, sp. gr. = 1.00748 at 18°. N. H. M.

Physiological Chemistry.

Digestion of Flesh in Normal Stomachs. By A. CAHN and v. MERING (*Bied. Centr.*, 1888, 352—353).—The acidity of the stomach juices is due solely to hydrochloric acid, which is present to the amount of 0·099—0·186 per cent. per hour (Human). In medium sized dogs, the quantity varies from 0·10—0·13 per cent. The percentage may rise after three hours to 0·39, and peptone may be present to the extent of 2·2 per cent. in one hour and 2·86 per cent. after two hours. After three hours, but little undissolved flesh meal can be found; consequently the author considers that the greater part of the albuminoids are peptonised in the stomach of a healthy animal before they pass to the duodenum. In spite of the variation in acidity, the total quantity of hydrochloric acid remains the same. Syntonin, although in small quantities, is found to the very end of the process, and the quantities of peptones rise in proportion to the acidity.

E. W. P.

Influence exerted by Sodium Chloride on the Digestion of Albumin in Fodders. By SIEVERT (*Bied. Centr.*, 1888, 315).—The results obtained are given in the following table:—

	Per cent. albumin.	Coefficient of digestion.			
		Without NaCl.	With 0·5 per cent. NaCl.	With 1 per cent. NaCl.	With 2 per cent. NaCl.
Coarse bran	13·82	84·51	87·30	83·86	78·28
Coarse bran previously deprived of fat.....	15·70	77·96	75·74	78·53	78·28
Fine bran	19·25	88·00	88·00	90·44	90·23
Rye bran	12·95	89·96	87·88	87·88	87·88
Rice meal (1).....	13·47	87·36	87·00	88·90	—
„ (2)	15·31	86·02	86·02	86·02	86·02
Palm-nut meal	16·54	75·90	—	75·40	—
Rape cake	30·89	85·85	85·85	86·80	86·90
Hemp cake	28·26	83·30	82·83	82·83	82·83
Cotton-seed cake	45·85	89·70	89·60	89·14	89·50
Earth-nut cake	45·15	94·35	94·00	93·60	94·30
Flesh-meal	69·32	94·30	—	94·20	94·20
Aftermath	13·40	71·50	71·80	72·91	72·91
Dried grains	21·61	74·30	73·73	74·30	74·30
Lupines	30·48	99·16	—	—	—
Lupines deprived of bitter principle	31·23	97·20	—	—	—

Stutzer's method was employed.

E. W. P.

Microchemical Observations on Hyaline Cartilage. By C. T. MÖRNER (*Zeit. physiol. Chem.*, **12**, 396—404).—The cartilage investigated was that of the trachea. Morochowetz, Landwehr, and Krukenberg have obtained gelatin from such cartilage, and a second substance, the investigation of which was the object of the present research. The existence of two substances in the ground substance can be demonstrated by the use of certain staining reagents. Methyl-violet, indigo-red, and a mixture of ferric chloride and potassium ferrocyanide stain a trabecular network which pervades the ground substance and is continuous with the perichondrium. This is composed of a collagenous material, from which gelatin is obtainable. The other substance occurs in spherical masses (chondrin balls), which surround the cells, and correspond in position with the cell capsules. This is not stained at all by the reagents previously mentioned, but is stained by indigo-blue and tropæolin, which do not affect the collagenous network. By the use of two staining reagents, one of each group, and applied to microscopic sections, double staining is obtained: for instance, with tropæolin and methyl-violet the network is stained yellow, the chondrin balls blue; with indigo-blue and aniline-red the network is stained blue, the chondrin balls red. It is the chondrin balls which have evidently been the second substance of other authors, the mucin of Morochowetz and v. Mering, the hyalogen of Krukenberg.

The chemical investigation of the chondrin balls shows them to consist of two substances, each differing from collagen and also from one another. The chemical separation of the constituents of the cartilage is accomplished by the use of dilute hydrochloric acid, and subsequently of dilute potassium hydroxide solutions. The former only diminishes the transparency of the sections; the latter dissolves out the chondrin balls. The chondrin is precipitated from its alkaline solution by acids, and also by certain metallic salts. Further details concerning the chemistry of these substances are promised. The present paper is concerned with histochemical details only.

W. D. H.

Lactic Acid of the Thymus and Thyroid. By R. MOSCATELLI (*Zeit. physiol. Chem.*, **12**, 416—418).—Gorup-Besanez (*Annalen*, **98**, 1) showed that the thymus and thyroid contain lactic acid, but which form of lactic acid has not yet been settled. Hoppe-Seyler's method (*Handbuch*, 109) of isolating the acid was employed with slight modifications. The water of crystallisation and the amount of zinc in the lactate of zinc prepared from both sources showed that the acid in question is paralactic acid.

W. D. H.

Production of Lactic Acid during Artificial Circulation of Blood through the Liver. By WISSOKOWITSCH (*Chem. Centr.*, 1888, 117—118, from *Arch. Physiol.*, **87**, 91).—Experiments were made to determine what change occurred in the amount of lactic acid in the blood during artificial circulation through the liver. Arterial and venous blood obtained from a suffocated animal, and serum were used. In all cases, with one exception, in the case of venous blood, the lactic acid was considerably increased, not infrequently to double the original

quantity present in the blood. Liver is more active in the production of lactic acid than either muscle, kidney, or lung. Neither the amount of oxygen nor the presence of blood corpuscles are necessary for the increased production of lactic acid. From the positive result obtained with serum, it was possible that the increase of lactic acid was due to a simple washing out of the liver, but an experiment with 0·7 per cent. sodium chloride solution showed that this was not the case. J. P. L.

Nitrogenous Constituents of the Contents of the Intestine which arise from the Body itself and not from Food. By V. HOFMEISTER (*Chem. Centr.*, 1888, 116, from *Arch. Thierheilkunde*, 14, 39—54).—To assume that the difference between the total proteïds ingested and the proteïds formed in the fæces strictly represents the proteïds digested would be an error, for the fæces contain, besides the undigested food material, the proteïds of the digestive fluids, epithelium of the digestive tract, mucus, and the nitrogen of the unabsorbed bile constituents. In order to estimate the limits of this error, the author has made a series of feeding experiments with pigs and horses on a purely non-nitrogenous (starch-paste) diet.

The amount of nitrogen expressed in terms of proteïd which arises from the above-mentioned causes in different parts of the alimentary canal varied during this diet very considerably. In the stomach, it varied from 0·17 to 14 per cent.; in the small intestine from 0·28 to 1 per cent.; and in the cæcum it was 0·65 per cent. The author explains how to apply corrections, and takes the opportunity to point out that during this starch diet the reaction of the cæcum contents was acid, whereas with other diets it was without exception alkaline. In the small intestine of the horse, too, the anterior portions were acid, whereas on other diets it was alkaline throughout. Sugar was almost completely absent from the stomach and small intestine, but present in the cæcum and even in the colon. This anomaly is explained from the want of amylolytic ferment in the food and from the very small secretion of saliva with this diet. In the cæcum, where the food remains some time, and where it meets with amylolytic ferments in its own secretions, sugar is formed, and it is to the formation of lactic acid from this sugar that the acid reaction of the cæcum is ascribed. J. P. L.

Variations in the Fat of Milk. By L. F. NILSON (*Bied. Centr.*, 1888, 171—183).—The author examined the milk of a herd of 15 cows in Sweden for the space of a year, making separate determinations in the case of each individual cow and of the morning's and evening's milk. These determinations were made every sixth day, and in some cases more frequently, and consisted in the estimation of the fat by Soxhlet's areometric method and of the volatile acids in the fat by a method giving relative values. He found, with but few exceptions, that the evening's milk was richer in fat than the morning's milk. The former gave 3·82 per cent. of fat and the latter 3·33 per cent. as an average of the whole year. As regards volatile acids, the fat of colostrum contained an unusually small amount; the

amount then rose rapidly, reaching a maximum in from five to seven days from calving; at this height, it remained for a short time, and then slowly fell until the end of the period of lactation.

The difference between summer and winter butter, depending on the amount of low melting glycerides, is usually ascribed to pasturing and fodder, but the author believes it to be due rather to the fact that the cows are usually in the pastures and receiving green fodder at the earlier part of their period of lactation.

The author found that the volatile acids were larger in amount in the fat of morning's than of evening's milk from November to March, that in April the difference disappeared, that during the spring and summer it was very small, and that it reappeared in the autumn. This he ascribes to the darkness of the Swedish autumn and winter nights, and the lightness of those of the spring and summer.

H. H. R.

Changes in the Composition of Milk. By H. FABER (*Bied. Centr.*, 1888, 316—317).—Examination of very numerous milk analyses shows that the dry matter minus fat remains constant (8·7 to 8·8), but that the fat alone varies. Evening milk contains most fat, as also does that produced in October and November.

E. W. P.

General Method of obtaining Non-organised Ferments in pure Aqueous Infusions. By N. KRAVCOFF (*J. Russ. Chem. Soc.*, 1887, 387—392).—The non-organised ferments, together with albuminoids, are precipitated by ammonium sulphate. By treatment with alcohol, the albuminoids become insoluble, and the ferments can then be extracted with water. From human saliva, the ferment was obtained as follows: the saliva was mixed with an equal volume of water, and finely-powdered ammonium sulphate was added to complete saturation, leaving some of the salt undissolved. After filtration, the precipitate was boiled for five minutes with strong alcohol, in order to render it more compact and easier to remove from the filter; it was then placed in absolute alcohol from 1 to 1½ days. After carefully decanting the alcohol, the precipitate was dried at 30°, and then extracted with a volume of water equal to that of the original saliva. On filtration, a clear liquid was obtained, showing but a slight opalescence, and quite free from albuminoid or mucous substances. At 40°, a turbid starch solution is rendered clear at once. Fehling's test is reduced. This ferment infusion loses its activity in the air, whereas in an atmosphere of carbonic anhydride or chlorine, its hydrolytic property remains unaltered. In the same way, an infusion of trypsin (better pancreatin) was obtained from the salivary gland of a dog's stomach, or the stomach of a calf or pig; it was found that the pancreas infusion obtained from the dog had the most energetic action, that from the calf being the most feeble. The filtrates from the quasi-mechanical precipitation with ammonium sulphate contain no active ferment, and the above pure ferment infusion, on addition of ammonium sulphate, becomes turbid, and the flocks which separate, after being treated in the same manner as the precipitates obtained from saliva, give extracts with the same

hydrolytic (saccharifying) properties as the above infusions, whilst the filtrates are found to be inactive. B. B.

Active Oxygen in Living Tissue. By C. WURSTER (*Ber.*, **21**, 1525—1528).—A reply to Bokorny (this vol., p. 751), in which the author gives further evidence in support of his views. Many vegetable juices oxidise more strongly than a centinormal iodine solution. The saliva of healthy, fair, young men quickly oxidises ammonia in glacial acetic acid solution to nitrous acid. For reasons previously stated the oxidising substance in vegetable juices must be either nitrous acid or hydrogen dioxide, and although hundreds of juices show this strong oxidising action, nitrous acid could not be detected, by means of Griess' reagents, in a single case. F. S. K.

Furfuraldehyde Reactions. By L. v. UDRÁNSZKY (*Zeit. physiol. Chem.*, **12**, 377—395; compare this vol., pp. 180 and 878).—The question whether normal urine contains carbohydrates has been one on which a large amount of work has been done, but has never been satisfactorily settled. The most recent of these observations are those of Landwehr (*Abstr.*, 1887, 26, this vol., p. 175), who states that animal gum may be present in the urine, and the author's own researches on humous substances (this vol., p. 180). The fact that carbohydrates yield furfuraldehyde on treatment with acid, which can be identified by means of the characteristic colour given with bile acid, α -naphthol, and many other substances, has led to the present reinvestigation of the question. The special method adopted is that of H. Schiff (*Ber.*, **20**, 540), in which strips of filter-paper are dipped in a mixture of xylydine, glacial acetic acid, and alcohol, then dried. The substance suspected to contain carbohydrate is heated in a tube with sulphuric acid; the fumes, which contain furfuraldehyde, strike a red colour with the strips of paper placed at the mouth of the tube. Using this method with quite small quantities (a few drops) of normal urine, the colour never fails to appear. The conclusion is drawn that normal urine contains carbohydrates, although of what kind is doubtful. A reaction described by Molisch, in which either thymol or α -naphthol and sulphuric acid give a red coloration, may also be used with the same result.

In cases of glycosuria these reactions occur more readily, and by a minutely described process of appropriate dilution of the urine, an approximate quantitative result may be obtained, at least sufficiently near to enable one to say whether the secretion contains more than a normal amount of carbohydrate.

In all such testing, the urine must be free from proteid, as the concluding portions of the paper show that furfuraldehyde is one decomposition product of proteid; this fact is considered to be the first well-established chemical relationship between proteids and carbohydrates, although the physiological connection between the two classes of substances has been long recognised (Bernard, Seegen, &c.). It also affords an explanation of the colour reactions which are caused by treating proteid with acid, such, for example, as the Adam-

kiewicz reaction. The amido-acids which result from the decomposition of proteïds yield no furfuraldehyde. W. D. H.

Pathological Pigments. By E. NEUMANN (*Chem. Centr.*, 1888, 227—228, from *Virch. Arch.*, **111**, 25—47).—(1.) *Origin of Hæmatoidin and Hæmosiderin in Extravasations and Thrombi.*—All observations lead to the conclusion that hæmosiderin arises only from those blood corpuscles which are in intimate contact with, or penetrate into the tissue, and that hæmatoidin arises from blood corpuscles which remain in the coagulum outside the tissue; for the formation of hæmosiderin, the action of the living tissue or its cells is necessary, whilst the formation of hæmatoidin is not conditional on the vital activity of tissue, but on chemical decomposition. (2.) *Pseudomelanose.*—The black pigment grains of pseudomelanose are, like hæmosiderin granules found almost exclusively within the cellular elements.

The change of iron pigments from rusty-brown to black when putrefaction sets in, favours the assumption that pseudomelanotic pigmentation of tissue is brought about by a combination of pathological and cadaveric processes. J. P. L.

Physiological Action of Cocaine. By MOSO (*Arch. Pharm.* [3], **26**, 179, from *Ann. Chim. Farm.*, 1887, 326).—The author finds experimentally that cocaine is the best cerebro-spinal stimulant. If an animal sleeping from a fatal dose of chloral hydrate be injected with 0.01 to 0.02 gram of cocaine per kilo. of body-weight, the rate of breathing and pulsation is increased, and the animal awakes, although the low temperature induced by the chloral hydrate continues. Conversely, the action of 0.046 gram of cocaine per kilo. of the body-weight is neutralised by 1.5 grams of chloral hydrate; cocaine may therefore prove to be efficacious in the case of poisoning by means of opium, morphine, and other narcotic substances, which strongly depress the nerve-centres governing respiration and the heart's action. J. T.

Behaviour of Benzoic Anhydride in the Organism. By E. SALKOWSKI (*Chem. Centr.*, 1887, 186, from *Centr. Med. Wiss.*, **25**, 161—163).—Benzoic anhydride shows the same marked antiseptic properties as the acid; when it is digested with finely minced meat or albumin at 40°, it is converted into the acid, but no sepsis occurs. Digestive ferments cause the same change. Taking benzoic anhydride does not induce any evident disturbance; it is changed into benzoic acid, and excreted in the urine as hippuric acid. The antiseptic action in the intestine is shown by the diminution in the amount of ethereal sulphates which occurs in the urine. Its action on the proteïd metabolism in dogs is small, and not greater than the action of benzoic acid or sodium benzoate. J. P. L.

Behaviour of Orthohydroxyquinolinecarboxylic Acid and its Derivatives in the Organism. By S. KRÓLIKOWSKI and M. NENCKI (*Monatsh.*, **9**, 208—216).—Orthohydroxyquinolinecarboxylic

acid has no injurious action on rabbits when administered subcutaneously in doses of 1 gram of the sodium salt. Daily doses of 2 to 4 grams were given to a dog weighing 12 kilos. without any injurious effect. The animal's urine was deep yellow, showed an acid reaction, and gave the same deep brownish-red coloration with ferric chloride as orthohydroxyquinolinecarboxylic acid. Part of the acid separated unchanged when the urine was evaporated, and a further quantity was obtained when the filtered urine was acidified with acetic acid, and treated with cold alcohol. The greater part of the acid had therefore passed unchanged, and no new product could be detected, neither was the formation of ethereal sulphates increased to any appreciable extent.

Methyltrihydro-orthohydroxyquinolinecarboxylic acid has no injurious effect on dogs in doses of 2 grams daily, nor has it any deleterious action on man when taken in doses of 1 gram from 4 to 5 times daily. The urine shows the same deep-red coloration with ferric chloride as the free acid; when it is evaporated, extracted with alcohol, and the alcoholic extract evaporated to a syrup, acidified with hydrochloric acid, and shaken with ether, a crystalline precipitate of unchanged methyltrihydrohydroxyquinolinecarboxylic acid (70 to 80 per cent.) separates after a time.

Methyldihydrodihydroxyquinolinecarboxylic acid,



is present in very small quantities in the ethereal extract. It crystallises in rhombic needles and prisms melting at $254-255^\circ$, is almost totally insoluble in water, but readily soluble in alcohol, ether, and alkalis, and gives a blue coloration with ferric chloride. Acids precipitate it from its solution in alkalis as a white, amorphous compound. This compound is formed to a somewhat larger extent in the human than in the canine organism.

The quantity of the ethereal sulphates in urine is not increased by doses of methyltrihydrohydroxyquinolinecarboxylic acid.

It seems that a small portion of tetrahydro-orthohydroxyquinolinecarboxylic acid is oxidised to the dihydrodihydroxy-acid in the animal organism.

F. S. K.

Reduction of Oxyhæmoglobin in Typhoid Fever. By A. HÉNOUCQUE and G. BAUDOUIN (*Compt. rend.*, 106, 1245—1248).—Periods of high temperature correspond with periods of diminished activity of reduction, and when the temperature is reduced, activity of reduction increases and tends to regain its normal value. A relapse, by producing an increase of temperature, immediately reduces the activity of reduction.

C. H. B.

Organic Chemistry.

Volatility of Poly-oxygen Carbon-compounds. By L. HENRY (*Compt. rend.*, **106**, 1089—1092).—A comparison of the boiling points of hydrocarbons, ketones, and polyketones shows that a double substitution of O for H_2 causes a much smaller proportional increase in the boiling point than a single substitution in the same part of the hydrocarbon-chain. The second substitution of O for H_2 in a hydrocarbon in the same portion of the chain as the first substitution causes a very much smaller rise in the boiling point. This is well shown by the following compounds:—

	B. p.		B. p.
Normal butane.	+ 1°	Normal pentane.	39°
Methyl ethyl ketone ..	78	Methyl propyl ketone .	101
Diacetyl	88	Acetylacetone	137
Hexane	68°		
Methyl butyl ketone ..	127		
Acetonylacetone	187		

In the butane series, the first substitution increases the molecular

weight 24.13 per cent., and the absolute boiling point 28.10 per cent., whilst the second substitution raises the molecular weight 19.44 per cent., but the boiling point only 2.84 per cent.

Methyl ethyl ketone and pentane have the same molecular weight, but the substitution of O for H_2 in the latter raises the boiling point 64° , but in the former only 10° .

It follows that the simultaneous presence of several oxygen-atoms in the same part of the molecule tends to reduce the boiling point.

C. H. B.

Volatility of Oxygenised Carbon-compounds. By L. HENRY (*Compt. rend.*, 106, 1165—1167).—The influence of oxygen in increasing the volatility of carbon-compounds is most strongly marked when two atoms of oxygen are directly united with one atom of carbon as in carbonic anhydride. The conversion of methane into carbonic anhydride increases the molecular weight by 175 per cent., but the absolute boiling point by only 77.06 per cent. When the two oxygen-atoms are united separately to different carbon-atoms, as in the group $—CO—CO—$; the latter, however, being in direct union with one another, the effect, although smaller, is still strongly marked. The conversion of normal butane into diacetyl raises the molecular weight 48.27 per cent. and the absolute boiling point 31.75 per cent. The volatilising effect is still evident when the two carbon-atoms are separated by a third carbon-atom as in the chain $—CO—CH_2—CO—$, but it disappears when two atoms intervene. The conversion of normal pentane into acetylacetone raises the molecular weight 38.88 per cent. and the absolute boiling point 32.25 per cent. Hexane and methyl propyl ketone have the same molecular weight, but the conversion of the former into acetylacetone raises the absolute boiling point 9.62 per cent., whilst the corresponding substitution in the hydrocarbon causes an increase of 17.30 per cent.

The volatilising influence of nitrogen is greater than that of oxygen, but it is affected to a much greater extent by separation of the carbon-atoms with which the nitrogen-atoms are united.

C. H. B.

Action of Feeble Bases on Nitroethane. By N. SOKOLOFF (*J. Russ. Chem. Soc.*, 1887, 384—387).—In a former paper, the author noticed that the action of ammonia in alcoholic solution on nitroethane gave rise to a compound, C_6H_5NO , and now he finds that a large quantity of ethaldehyde is formed at the same time. B. B.

Some Properties and Transformations of Dimethylallene (Reboul's Valerylene). By A. ALBITZKY (*J. Russ. Chem. Soc.*, 1887, 364—368).—Bromide of trimethylethylene (b. p. $115—125^\circ$) was prepared by the action of bromine on dimethyl ethyl carbinol, and this, by treatment with alcoholic potash, gave trimethylethylene. The bromide of trimethylethylene was heated in sealed tubes for 12 hours at 165° with thrice its bulk of alcoholic potash of 50 per cent., and some solid potash. The contents of the tubes, after being distilled on the water-bath, were decomposed by water, and the upper oily layer was washed with water, and dried over sodium sulphate. On repeated distillation over

caustic potash and metallic sodium, the hydrocarbon was obtained as a liquid boiling at $40.5-41.5^\circ$. The yield is one-third of the theoretical. It is *dimethylallene*, C_5H_6 . Its density (water at $4^\circ = 1$) at $0^\circ = 0.7525$, at $17^\circ = 0.6970$, at $20^\circ = 0.6940$. Coefficient of dilatation between 0° and $20^\circ = 0.0014$. Optical constants: $\frac{A-1}{d^{17}} = 0.57477$, $p \frac{A-1}{d^{17}} = 39.08$. Calculated, 34.62; difference, 4.46. Lorenz's formula, $\frac{A^2-1}{(A^2+2)^d} = 0.34829$, $p \frac{A^2-1}{(A^2+2)^d} = 23.68$. Calculated, 20.31; difference, 3.37. Two double linkings require a difference of 3.18. Oxidation with chromic mixture at the ordinary temperature after 25 days yielded acetone and acetic acid. The structure of dimethylallene is therefore $CMe_2:C:CH_2$. Sulphuric acid, sp. gr. 1.64, at the ordinary temperature yielded methyl isopropyl ketone and probably also divalerylene hydrate or trivalerylene. Dilute acid gives no better result.

B. B.

Isomeric Change of Hydrocarbons of the Acetylene Series by Heating them with Alcoholic Potash.

By A. FAVORSKY (*J. Russ. Chem. Soc.*, 1887, 414-427).—Methyl ethyl ketone was acted on with phosphorus pentachloride, and the chloride, $CH_3Me \cdot CMeCl_2$, obtained was heated in a sealed tube with alcoholic potash at 170° , a temperature which, according to Kutscheroff, is best adapted for the formation of ethylacetylene. The hydrocarbon obtained on distilling the contents of the tubes did not reduce ammoniacal silver or cuprous chloride solution, and when heated with sulphuric acid, crystals of hexamethylbenzene (m. p. 163.5°) were obtained. This shows that instead of ethylacetylene, $CH_3 \cdot CH_2 \cdot C:CH$, as expected, dimethylacetylene, $CH_3 \cdot C:C \cdot CH_3$, is formed; ethylacetylene is obtained, however, if dry potassium hydroxide is substituted for its alcoholic solution. When pure ethylacetylene is heated with pure ethyl alcohol, no isomeric change takes place, showing that alcohol alone has not caused the change. If, however, the hydrocarbon is heated for 16 hours at 170° with alcoholic potash, it will be found to be converted into dimethylacetylene, as is shown by the formation of hexamethylbenzene (m. p. 163.5°) when it is treated with sulphuric acid (5 to 1 water); ethylacetylene under these circumstances does not give hexamethylbenzene. These facts show that the isomeric change has taken place under the influence of alcoholic potash.

In order to subject propylacetylene to the action of alcoholic potash, the product of the action of phosphorus pentachloride on methyl propyl ketone, $CH_3 \cdot CCl_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$, was purified and heated with alcoholic potash at 120° . The propylacetylene, $CH_3 \cdot CH_2 \cdot CH_2 \cdot C:CH$, obtained, was purified by converting it into the cuprous compound, decomposing the latter with hydrochloric acid and distilling. The purified hydrocarbon was then heated with alcoholic potash at 170° , when it was found to be converted into the isomeric methylethylacetylene, $CH_3 \cdot CH_2 \cdot C:C \cdot CH_3$, which gives no precipitate with ammoniacal cuprous or silver solutions and boils at $55.5-56^\circ$. The same product

is obtained by the direct action of alcoholic potash at 170° on the chloride. On oxidation with chromic mixture, methylacetylene yields acetic and propionic acids; with sulphuric acid (1 water to 5 of acid), methyl propyl ketone was obtained, so that the above formula is confirmed. The isomeric change begins to take place at as low a temperature as $30-40^{\circ}$.

When isopropylacetylene, as a hydrocarbon of the acetylene series containing a secondary radicle, was heated with alcoholic potash at 150° , dimethylallene, $\text{CMe}_2\text{C}:\text{CH}_2$, was obtained; this was proved to be identical with that obtained from trimethylethylene. According to the author's theoretical views, a hydrocarbon of the acetylene series containing a tertiary group should not be altered by alcoholic potash. In order to prove this, hexoylene, $\text{CMe}_3\text{C}:\text{CH}$, was prepared from the dichloride from pinacolone by heating it with alcoholic potash at 140° ; the hydrocarbon boils at 39° , and gives both silver and cuprous compounds like a true acetylene. When heated with alcoholic potash, first for 8 hours at 170° , and then again for 16 hours at 200° , no alteration takes place. The isomeric change of monosubstituted acetylenes by the action of alcoholic potash is found to depend not only on their structure, but also on their molecular weight; caprylidene, for example, is obtained even at 150° (Béhal), whereas ethylacetylene and propylacetylene are easily converted into isomerides under the same conditions.

B. B.

Pyrrolylene Tetrabromides. By G. CIAMICIAN and G. MAGNANINI (*Ber.*, 21, 1430—1434).—The authors have repeated Ciamician and Magnaghi's work (*Abstr.*, 1886, 521), with the result that Grimaux and Cloez' conjecture (*Abstr.*, 1887, 789) as to the source of the pyrrolylene (erythrene) tetrabromide melting at $38-39^{\circ}$ is shown to be untenable. Pyrrolylene, obtained from erythrol, was brominated in the cold, and the product freed from excess of bromine by a current of air was extracted with light petroleum, in which Henninger's tetrabromide (m. p. $118-119^{\circ}$) is practically insoluble. On spontaneous evaporation of the solution, an oil was obtained which solidified in a freezing mixture, and, after removal of a small quantity of adhering oil, crystallised from light petroleum in colourless tables melting at $38-39^{\circ}$: hence the tetrabromide of lower melting point is a direct product of the bromination of pyrrolylene. The proportion in which the isomeric tetrabromides are formed is not always the same, and the quantity of the tetrabromide melting at $38-39^{\circ}$ obtained in these experiments was less than in those of Ciamician and Magnaghi.

Pyrrolylene tetrabromide (m. p. $118-119^{\circ}$) crystallises in monoclinic forms: $a : b : c = 2.63485 : 1 : 2.333815$; $\beta = 80^{\circ} 55'$. It is not converted into its isomeride by prolonged heating with excess of bromine at 100° , and when distilled at $180-181^{\circ}$ under 60 mm. pressure, yields a distillate from which traces only of the tetrabromide of lower melting point could be extracted by light petroleum.

W. P. W.

Action of Zinc Cyanide on Metallic Chlorides. By R. VARET (*Compt. rend.*, 106, 1080—1083).—A concentrated aqueous

3 g 2

solution of mercuric chloride is heated at 50—60° and mixed with pure zinc cyanide in quantity equal to about half the weight of the mercuric chloride. The liquid is then saturated with a further quantity of mercuric chloride, mixed with zinc cyanide in excess, filtered, and allowed to evaporate over sulphuric acid. The compound, $\text{ZnCy}_2, \text{HgCy}_2, \text{HgCl}_2 + 6\text{H}_2\text{O}$, separates in large, transparent, efflorescent, prismatic crystals, which become anhydrous at 100°; they are very soluble in water. When treated with gaseous ammonia, the compound becomes anhydrous and combines with 3 mols. of ammonia. When treated with aqueous ammonia, the crystals become white and dissolve with some development of heat; and when the solution cools, it deposits small, crystalline nodules of the compound $\text{ZnCy}_2, \text{HgCy}_2, \text{HgCl}_2, 6\text{NH}_3$, which loses ammonia when exposed to air, and is decomposed by water. It is slightly soluble in cold aqueous or alcoholic ammonia, and dissolves readily on heating.

When a solution of the first compound is mixed with potassium iodide, zinc cyanide is first precipitated, and afterwards mercuric iodide. By rapid manipulation, the zinc cyanide can be removed before the mercuric iodide separates. The presence of potassium iodide causes a reaction the reverse of that by which the compound was formed. Potassium iodide combines with mercuric cyanide, but not with zinc cyanide. If metallic copper is immersed in the ammoniacal solution, mercury is deposited, and the solution becomes blue. When concentrated, the liquid yields blue crystals which contain zinc, copper, and mercury. Copper does not displace mercury from mercuric cyanide, and from these results it follows that the compound has the constitution represented by the formula given, and cannot be regarded as a compound of mercuric cyanide with zinc chloride.

When zinc cyanide is added to a concentrated solution of cupric chloride, brown cupric cyanide is precipitated, heat is developed, and the cupric cyanide becomes cuprous cyanide with evolution of cyanogen. This reaction affords a convenient method for the preparation of pure cyanogen, and zinc cyanide has a great advantage over potassium cyanide in that it is not so liable to be contaminated with carbonate. When dry zinc cyanide and cupric chloride in equivalent proportions are heated together in an oil-bath, the evolution of cyanogen begins at about 150° and proceeds regularly at 160—170°. Zinc cyanide alone decomposes at about 300°.

Chlorides of the alkalis and alkaline earths, nickel, manganese, cobalt, iron, gold, platinum, &c., form no compounds with zinc cyanide, but yield a series of double salts with ammonio-zinc cyanide.

Zinc cyanide forms no double salts with metallic chlorides only.

C. H. B.

Action of Sodium on Homologues of Ethyl Cyanide. By E. v. MEYER (*J. pr. Chem.* [2], 37, 396—407).—The author has previously studied the formation and reactions of cyanethine and cyanmethine (Abstr., 1881, 54; 1883, 352, 653). *Cyanopropine*, $\text{C}_{12}\text{H}_{21}\text{N}_3$, is obtained by adding 77 grams of propyl cyanide to 8 grams of sodium in a retort closed with mercury; a violent action ensues, and propane is evolved. When all the sodium has disappeared, the

excess (23 grams) of cyanide is distilled off, and the residue washed with water, dried, and recrystallised from hot ether, which deposits it on cooling in pointed prisms. It melts at 115° , and is soluble in 1572 parts of water at 23° , forming a distinctly alkaline solution. Its platinochloride crystallises in slender, yellow-red prisms melting at 97° . By heating cyanopropine with concentrated hydrochloric acid at 180° for some hours, and then neutralising with sodium hydroxide, a hydroxy-base, $C_{12}H_{19}N_2 \cdot OH$, is obtained in slender needles; this melts at 97.5° , and is soluble in 1497 parts of water at 23° ; it is easily soluble in alkalis, and gives an amorphous silver salt, $C_{12}H_{19}AgN_2O$, when a mixture of its solution with silver nitrate is neutralised with ammonia.

Bromocyanopropine crystallises as its hydrobromide, when an acid solution of cyanopropine is evaporated with bromine, and from this it may be obtained on the addition of ammonia. It forms needles melting at 80° . During the action of the bromine, an oil is obtained which behaves with ammonia like the similar product from cyanethine and bromine (Abstr., 1883, 353), giving a sparingly soluble amide of symmetrical diethylsuccinic acid.

Isopropyl cyanide acts very violently on sodium, yielding a slimy, brick-red mass, which, after the excess of the cyanide has been distilled off, is treated with water, whereupon it evolves ammonia, leaving a disagreeably smelling oil undissolved. This oil partially crystallises after a time; recrystallisation from benzene gives slender needles of the composition $C_{19}H_{34}N_6$, melting about 241° ; the platinochloride forms thin, yellow prisms sparingly soluble in water and containing $2\frac{1}{2}$ mols. H_2O , of which $1\frac{1}{2}$ mols. are retained at 170° . The portion of the oil that does not crystallise gives off isopropyl cyanide and water at 87° ; treatment of the residue with concentrated hydrochloric acid at 60° gives an oil, which may be extracted by ether, and an acid solution. The dried oil gives two fractions which are split up into isobutyric acid and ammonia by acid and alkalis, and a third from which di-isobutyramide (Abstr., 1882, 950) is obtained by the action of concentrated hydrochloric acid. The acid solution from which the oil was extracted contained ammonium isobutyrate, and gives a mixture of oils when neutralised with potassium hydroxide; when this mixture is treated with concentrated hydrochloric acid at 190° , ammonium chloride is formed, and by distilling the acid liquid with excess of alkali, it yields a base. This base, $C_{12}H_{22}N_2$, forms silky needles melting at $136-137^{\circ}$, subliming in prisms at 100° , sparingly soluble in water to a distinctly alkaline solution, freely soluble in alcohol and ether. Its platinochloride, $(C_{12}H_{22}N_2)_2 \cdot H_2PtCl_6$, forms thin, yellow prisms; and its silver nitrate compound, $(C_{12}H_{22}N_2)_2 \cdot AgNO_3$, a voluminous, white precipitate. By oxidation with permanganic acid, the base is converted into di-isobutyramide, ammonia, carbonic anhydride, isobutyric acid, and isopropyl cyanide.

A. G. B.

Action of Sodium on Isobutyl Cyanide and Isoamyl Cyanide.

By J. TROEGER (*J. pr. Chem.* [2], 37, 407-411).—*Cyanobutine*, $C_{15}H_{27}N_3$, is obtained when 40 grams of isobutyl cyanide and 4 grams of sodium are gently heated together in a retort until action begins. A gas, probably trimethylmethane, is evolved; the residue is after-

wards treated with water. The undissolved resin is dissolved in ether, and hydrogen chloride passed through the solution. The hydrochloride thus formed is decomposed by alcoholic ammonia, and the resulting oil extracted by ether; the ether is evaporated, and leaves an oil which gradually crystallises in stellate groups. A *hydroxy-base*, $C_{15}H_{25}N_2 \cdot OH$, is obtained by heating cyanobutine with hydrochloric acid, or by passing nitrous anhydride through a solution of it in glacial acetic acid, and adding ammonia, when it is precipitated as an oil, which crystallises on cooling, and melts at $88-89^\circ$.

Methylcyanobutine hydriodide, $C_{15}H_{25}MeN_3 \cdot HI$, is obtained when cyanobutine is heated with methyl iodide at 160° .

Cyanamyline, $C_{18}H_{33}N_3$, is obtained by heating 40 grams of isoamyl cyanide with 3.5 grams of sodium; after distilling off excess of the cyanide and washing with water, the residue is dissolved in alcohol; on dilution with water the base is thrown down as an oil, crystallising gradually. The crystals are purified by distillation. Cyanamyline is a strong base, melting at 53° .

A *hydroxy-base*, $C_{18}H_{31}N_2 \cdot OH$, is obtained when nitrous anhydride is added to the solution of cyanamyline in glacial acetic acid. It forms long, white needles, and has only feebly basic properties.

A. G. B.

Formation of Cyanethine from Ethyl Cyanide. By E. v. MEYER (*J. pr. Chem.* [2], **37**, 411—413).—In this preliminary paper the author reverts to his previous work (*Abstr.*, 1881, 54). Cyanethine is not obtained by the action of sodium on an ethereal solution of ethyl cyanide, but a white powder is formed, which partially dissolves in water, and from the solution an oil separates, which eventually crystallises. This new substance is a polymeride of ethyl cyanide; it melts at $47-48^\circ$, and boils between 257° and 258° unchanged; it has hardly any basic properties, and is converted by acids into ammonia and a limpid oil containing nitrogen, which has a strong reducing action on silver nitrate. Sodium acts energetically on this polymeride when heated with it, forming ethyl cyanide, which is partially converted into cyanethine. The author and others are trying the action of sodium on ethereal solutions of other alkyl cyanides.

A. G. B.

Tertiary Ethyl Amyl Ether. By J. KONDAKOFF (*J. Russ. Chem. Soc.*, 1887, 300—301).—Tertiary amyl ethyl ether is obtained as a bye-product when trimethylethylene is prepared from tertiary amyl iodide by Boutleroff's method. It remains dissolved in the alcoholic potash, and may be separated by the addition of water; the yield is very small, 20 grams only having been obtained from 900 grams of iodide. It boils at 102° , and is a light, mobile liquid of sp. gr. 0.7785 at 0° , and 0.751 at 18° . As it yields ethyl iodide and tertiary amyl iodide when treated with hydriodic acid, its constitution is $C_5H_{11} \cdot OEt$. The ether has been already described by Réboul (*Compt. rend.*, **64**, 1243), but as in Beilstein's *Handbuch*, the name of ethyl amyl ether is given to the ether of methyl isopropyl carbinol, the author has tried to prepare his ether synthetically from tertiary amyl iodide

and sodium ethoxide; the yield, however, was very small. The same compound was prepared from the iodide of methyl isopropyl carbinol and sodium ethoxide, but in both reactions large quantities of trimethylethylene were obtained. B. B.

Action of Halogen Hydrides on Oxymethylene. By W. TISHTCHENKO (*J. Russ. Chem. Soc.*, 1887, 464—478).—In 1883, the author found that on heating oxymethylene with aqueous halogen acids, formic acid was formed, together with halogen-derivatives of methane. In order to study this reaction, in which both water and the halogen hydride seem to take a part, the author has heated oxymethylene with water for several days in sealed tubes at 115°. The product of the reaction contained no formic acid, and the reaction was therefore not analogous to that which takes place with halogen acids, for only a little methyl alcohol was formed, as it would seem owing to the presence of alkalis from the glass. When oxymethylene was heated with very weak halogen acids, it remained nearly unaltered even for weeks, and only very small quantities of methyl chloride and formic acid were found among the products of reaction. In order to study the action of dry halogen hydrides on oxymethylene, an apparatus was employed, which could be weighed. After bringing in dry oxymethylene, dry hydrogen iodide was passed over it, when a reaction accompanied by the development of heat began, so that after 30 minutes the oxymethylene disappeared; the hydride, however, does not cease to be absorbed until after 12 to 16 hours. The product of the reaction consists of two layers, of which the upper is aqueous hydriodic acid, and the lower a liquid, boiling at 219°, and having the composition $C_2H_4I_2O$, that is, the di-iodated methyl ether, the formation of which the author represents by two phases: (a) $CH_2O + HI = CH_2I \cdot OH$, and (b) $2CH_2I \cdot OH = CH_2I \cdot O \cdot CH_2I + H_2O$. Hydrogen bromide yields the analogous compound $C_2H_4Br_2O$, boiling at 148·5—151·5°. In contrast to the hydrogen bromide and iodide, the action of hydrogen chloride is very slow, as 20 grams of oxymethylene, even after six to seven days, was only partially transformed into the compound $C_2H_4Cl_2O$, an oily liquid boiling at 102—108°.

All three halogen compounds are oily liquids of an extremely pungent odour, affecting the eyes and nose; insoluble in water, but decomposed by and fuming in the air. They are soluble in ether, benzene, and acetone. Their structure is symmetrical, for the action of water corresponds quantitatively with the reaction $CH_2Br \cdot O \cdot CH_2Br + H_2O = 2CH_2O + 2HBr$, and no formic acid is produced. On heating the compound $C_2H_4Br_2O$ with water and oxymethylene at 140°, methyl bromide and formic acid were formed, from which the author concludes that the formation of formic acid and methyl haloids (monohaloid derivatives of methylene) on heating oxymethylene with aqueous halogen acids, is due not to oxidation or to reduction of 2 mols. of the oxymethylene, but to the reaction between 1 mol. of oxymethylene and 1 mol. of a haloid hydrin of methylene glycol, the last being the product of the reaction of the halogen hydride on oxymethylene. B. B.

Action of Halogens on Oxymethylene. By W. TISHTCHENKO (*J. Russ. Chem. Soc.*, 1887, 479—483).—The action of chlorine on oxymethylene is very simple, consisting in the substitution of chlorine for hydrogen. A large flask was used, and it was found that the temperature had no perceptible influence. In direct sunlight, however, the reaction is very rapid, and is represented by the equation $\text{CH}_2\text{O} + 2\text{Cl}_2 = \text{COCl}_2 + 2\text{HCl}$. The action of bromine is not quite so simple. It was best effected in sealed tubes at 100° . Carbonic oxide and anhydride escaped after opening the tube, and a liquid remained, which consisted of the bromide $\text{CH}_2\text{Br}\cdot\text{O}\cdot\text{CH}_2\text{Br}$, methyl bromide, hydrobromic acid and formic acid. The action of iodine on oxymethylene at 125° is analogous. B. B.

Action of Zinc Organic Compounds on Oxymethylene: Synthesis of Primary Alcohols. By W. TISHTCHENKO (*J. Russ. Chem. Soc.*, 1887, 483—486).—Wagner has found that aldehydes with zinc organic compounds yield secondary alcohols, and as oxymethylene may be regarded as an aldehyde containing a hydrogen-atom in place of an alkyl group, the formation of primary alcohols might be expected to take place. From zinc ethide and oxymethylene, after decomposition of the product of reaction by water, propyl alcohol was obtained, and in like manner normal butyl alcohol was formed when zinc propide was used.

The following method for the preparation of oxymethylene is recommended by the author:—The mixture of air and methyl alcohol vapour must be passed over platinised asbestos containing not too much platinum, and this must be placed loosely in the tube, otherwise the alcohol would be oxidised to carbonic anhydride. The temperature of the exit part of the tube only is to be kept below red heat, the part of the tube with the asbestos where the vapour enters being heated by the heat of the reaction itself. The current of air passed through methyl alcohol should be pretty rapid, but yet so that the individual bubbles are still distinguishable. When the solution obtained is placed in an exsiccator under reduced pressure over sulphuric acid, and this acid often renewed, 13·17 per cent. of dry oxymethylene remains after several weeks. It is perfectly dry and powdery if the solution be repeatedly stirred during the drying.

B. B.

Ethylene Disulphides and Ethylene Disulphones. By H. FASBENDER (*Ber.*, 21, 1473—1477; comp. Abstr., 1887, 462).—*Ethylidene ethylene disulphide*, $\text{CHMe} < \begin{smallmatrix} \text{S}\cdot\text{CH}_2 \\ \text{S}\cdot\text{CH}_2 \end{smallmatrix} >$, is a colourless oil boiling at 172 — 173° . The corresponding *disulphone* crystallises from water in needles which melt at 198° , and volatilise on further heating.

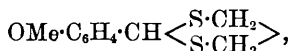
Propylidene ethylene disulphide, $\text{CHEt} < \begin{smallmatrix} \text{S}\cdot\text{CH}_2 \\ \text{S}\cdot\text{CH}_2 \end{smallmatrix} >$, boils at 191 — 192° . The *disulphone* melts at 124° .

Ethylene mercaptan also condenses with valeraldehyde, and with

chloral it forms an additive product, $C_2H_4[S \cdot CH(OH) \cdot CCl_3]_2$, which crystallises from ether in shining silky leaves melting at 116° .

Benzylidene ethylene disulphide, $CHPh \langle \begin{smallmatrix} S \cdot CH_2 \\ S \cdot CH_2 \end{smallmatrix} \rangle$, melts at 29° , and dissolves in concentrated sulphuric acid with a deep orange-yellow colour.

Paramethoxybenzylidene ethylene disulphide,



obtained from anisaldehyde and ethylene mercaptan, forms colourless needles melting at $64-65^\circ$.

Glyoxalethylenemercaptale, $C_2H_4S_2 \cdot CH \cdot CH \cdot C_2H_4S_2$, forms flat, feathery leaves which melt at 133° , and sublime without decomposition. It is readily soluble in alcohol, sparingly in ether, and insoluble in water. When carefully oxidised with nitric acid in glacial acetic acid solution, it is converted into ethylenedisulphonic acid. *Dimethylmethylethylene disulphide*, prepared by treating acetone and mercaptan with hydrochloric acid, is a colourless oil boiling at 171° . *Dimethylene ethylene disulphone*, $CMe_2 \langle \begin{smallmatrix} SO_2 \cdot CH_2 \\ SO_2 \cdot CH_2 \end{smallmatrix} \rangle$, is obtained by oxidising the preceding compound with potassium permanganate in acetic acid solution. It crystallises in needles which melt at 232° , and distil without decomposition.

Diphenylmethylethylene disulphide, $CPh_2 \cdot S_2 \cdot C_2H_4$, crystallises from alcohol in long, broad plates melting at 106° .

Ethylenemercaptandipyrvic acid, formed by mixing the mercaptan with pyruvic acid, crystallises from benzene in the form of a white, crystalline powder which melts at 96° , and is slowly decomposed on exposure to the air.

Ethylenemercaptalepyruvic acid, $COOH \cdot CMe \cdot S_2 \cdot C_2H_4$, obtained by the condensation of the preceding compound, separates from alcohol, ether, and chloroform, in clusters of short crystals melting at 102° . The *silver* salt forms colourless needles which become violet-red on exposure to the air. The acid yields ethylidene ethylene disulphone, melting at 198° when oxidised.

F. S. K.

Diethylene Tetrasulphide. By H. FASBENDER (*Ber.*, **21**, 1470—1472; compare *Abstr.*, 1887, 462).—Diethylene tetrasulphide can be obtained by the action of the halogens on ethylene mercaptan in chloroform solution; also by treating the mercaptan with concentrated sulphuric acid, or with sulphuryl chloride. Furthermore by acting on an alkaline solution of the mercaptan with hydroxylamine hydrochloride. Hydroxylamine hydrochloride acts similarly on alkaline solutions of ethyl mercaptan, phenyl mercaptan and thioresorcinol.

Diethylene tetrasulphide softens at 141° , melts at $151-152^\circ$, and is not decomposed either when heated alone at 200° , or when heated with phenol. When treated with bromine, it yields an additive product, $C_4H_8S_4Br_2$, which forms well-defined, brownish-red unstable crystals.

F. S. K.

Action of Feeble Mineral Acids on Allyl Alcohol. By W. SOLONINA (*J. Russ. Chem. Soc.*, 1887, 302—315).—Livoff and Shishukoff have shown that the action of acids converts the unsaturated alcohol, isobutenol, C_4H_8O , into its isomeride isobutaldehyde, and that isobutylene glycol is formed at the same time as an intermediary product. It was interesting to investigate the first homologue of this series, allyl alcohol, in the same direction, especially as but little was known as to the action of acids on allyl alcohol up to this date.

One volume of allyl alcohol was heated with two volumes of hydrochloric acid (containing 10 per cent. of HCl) for about 20 hours at 100° . After the lapse of this time, the tubes were found to contain one-eighth to one-tenth of a brown oily liquid, the remainder being a brownish-yellow, aqueous liquid. On repeating the process, more of the oily liquid was obtained. The oily liquid was distilled with aqueous vapour in a current of carbonic anhydride in order to prevent the absorption of oxygen. After washing with water in the presence of marble, and drying over calcium chloride, the different fractions were investigated. Fraction $45\text{--}46^\circ$ was found to be allyl chloride. Fraction $94\text{--}95^\circ$ was allyl ether. Fraction $135\text{--}138^\circ$ was a pale-yellow oil of a pungent odour, absorbing oxygen eagerly. It exhibited the general properties of unsaturated aldehydes; its dibromide is very unstable; its formula, $C_6H_{10}O$, was confirmed by several vapour-density determinations. The oil was then subjected to the action of a continuous current of oxygen; this was absorbed and carbonic anhydride evolved. After purification, the product was boiled with calcium carbonate, and the unaltered portion distilled off. The residue, when crystallised from dilute alcohol, gave a calcium salt, $(C_6H_9O_2)_2Ca + 4H_2O$; the silver salt is $C_6H_9O_2Ag$. Both are salts of α -methyl- β -ethacrylic acid. The hydroxylamine-derivative C_6H_9NO was prepared by the action of sodium carbonate and hydroxylamine hydrochloride in a feeble alcoholic solution. After extraction with ether and recrystallisation from light petroleum, crystals were obtained melting at $48\text{--}49^\circ$, and boiling without decomposition at $193\text{--}194^\circ$. A vapour determination confirmed the above formula.

The author thinks that the aldehyde obtained by him is the α -methyl- β -ethacraldehyde, $C_2H_5\cdot CH:CMe\cdot CHO$, of Lieben and Zeisel (*Abstr.*, 1883, 570). The aqueous layer was distilled over potassium carbonate, and the distillate contained a small quantity of propaldehyde together with allyl chloride. From the remaining aqueous portion, after evaporation, filtration, &c., an oily liquid was obtained, boiling between 180° and 194° , which was found to be propylene glycol. The action of dilute sulphuric acid is analogous to that of hydrochloric acid.

B. B.

Isodulcitol. By E. FISCHER and J. TAFEL (*Ber.*, 21, 1657—1660; compare this vol., p. 39).—*Isodulcitolcarboxylic acid*, $C_7H_{14}O_7$, is formed when 25 grams of isodulcitol dissolved in 25 c.c. of water is heated with 7.5 c.c. of anhydrous hydrogen cyanide at 30° ; after one and a half hours, the whole is cooled and kept for 12 hours at the ordinary temperature. It is again heated at 30° for some hours, diluted with water and evaporated down. The residue is then heated

with an excess of baryta-water on a water-bath, dissolved in much water, treated with carbonic anhydride, and decolorised with animal charcoal. On evaporating down, the *barium salt* separates in colourless, slender plates. The yield of pure salt is 15.5 grams. The free acid could not be isolated, as it is converted into the *lactone*, $C_7H_{12}O_6$, when the acid solution is evaporated. The latter crystallises in slender, concentrically grouped needles, melts at 168° , dissolves readily in water and alcohol, very sparingly in ether. When the barium salt is reduced with hydriodic acid and amorphous phosphorus, an oil is obtained having the properties of a fatty acid.

N. H. M.

Perseite. By MAQUENNE (*Compt. rend.*, **106**, 1235—1238).—The perseite employed was extracted from the stones of the ripe fruit of *Laurus persea*, which gave about 15 grams per kilo. No saccharose was present, but the stones contained a small proportion of reducing sugar identical in properties with invert sugar.

Pure perseite melts at 188° , and is sensibly volatile. It has the composition $C_6H_{11}O_6$, and the molecular weight as determined in aqueous solution by Raoult's method is 179. The formula corresponds with 182.

The *hexacetate*, $C_6H_8O_6(C_2H_3O)_6$, is obtained by dissolving the perseite in five times its weight of boiling acetic anhydride and a fragment of zinc chloride, and recrystallising the product from alcohol. It forms a white crystalline powder, which has a somewhat bitter taste, and is insoluble in water, but dissolves in alcohol. It melts at 119° , and volatilises at a higher temperature. The *hexabutyrate*, obtained by the action of butyric chloride, is a viscous, yellowish liquid, insoluble in water, but soluble in alcohol or ether. It boils at about 300° in a vacuum with gradual decomposition. The *hexanitrate*, $C_6H_8O_6(NO_2)_6$, is obtained by adding sulphuric acid to a cold solution of perseite in nitric acid, washing the product with water, and recrystallising from alcohol of 95° . It crystallises in light, slender needles, insoluble in water, and only slightly soluble in alcohol. It softens at about 132° , and melts distinctly at 138° . At higher temperatures, it gives off nitrogen oxides. If heated rapidly, it melts without exploding, but it detonates under the hammer, although less violently than nitromannitol or nitroinosite.

All these derivatives yield perseite when treated with alkalis. It is evident that perseite is a hexahydric alcohol, and a true isomeride of mannitol and dulcitol.

C. H. B.

Products of the Action of Red Mercuric Oxide and Baryta-water on Glucose. By A. HERZFELD (*Annalen*, **245**, 27—35).—The chief product of the action of red mercuric oxide and baryta-water on glucose is gluconic acid. Glycollic and formic acids are also formed, but the presence of glyceric and trihydroxybutyric acids could not be detected.

W. C. W.

Anilides of Glucoses and some of their Transformations. By V. SOROKIN (*J. Russ. Chem. Soc.*, 1887, 377—384).—The crystalline anilides of galactose, levulose and dextrose have been

already described by the author (Abstr., 1886, 526, 683). Formerly the author heated the glucoses with aniline to its boiling point, but now he finds that the quantity of brown decomposition products formed is much smaller if the temperature is kept at 130—135°, so that the glucose is just dissolved. Still better results are obtained in alcoholic solution. For 10 grams of pure glucose, 26 grams of aniline, and 150 c.c. of alcohol of 98 per cent. are taken, and the liquid boiled until dissolution of the glucose is complete. When half the liquid has been distilled off and the residue cooled, the anilide crystallises out, especially on the addition of 2 to 3 volumes of ether. After recrystallisation from alcohol, 80 per cent. of the theoretical quantity is obtained. Methyl alcohol may be used instead of ethyl alcohol. In order to prepare the anilide of galactose, alcohol of 90 per cent. is employed, and the operation conducted as above. The preparation of the anilide of lævulose is far more difficult, a large quantity of a syrup and only a small quantity of the crystalline anilide being obtained. The separation of the latter from the former is effected by taking advantage of its solubility in alcohol. The galactose-anilide crystallises in long triclinic prisms, lævulose-anilide in rectangular plates, dextrose-anilide is only with difficulty obtained in small needles. Pure dextrose-anilide becomes brownish on heating to 140°, and melts at 147°, solidifying to a dark, vitreous mass. Its formula, $C_{12}H_{17}NO_5$, corresponds with that of its analogues. As the aqueous solutions are easily decomposed, the specific rotatory power was determined in methyl and ethyl alcoholic solution. All the solutions were found to be *levogyrate*, so that when the aniline-residue enters a glucose molecule, the dextrogyrate power is converted into the levogyrate in the case of galactose and dextrose, whereas that of lævulose is increased merely. The rotatory power of lævulose-anilide in alcoholic solution increases with decreasing concentration. When to an aqueous solution containing 2 to 3 per cent. of either anilide at 0° bromine is added, until the precipitate formed is coloured red, and the filtrate is subsequently treated with silver oxide and hydrogen sulphide, the corresponding glucoses are formed, and the insoluble precipitate is found to be symmetrical tribromanilide. By the action of nitric acid, the anilides are split up into glucoses and aniline, but the former are at once oxidised. From dextrose-anilide a small quantity of saccharic acid is obtained. Galactose-anilide yields mucic acid.

B. B.

Fermentation of Galactose. By B. TOLLENS and W. E. STONE (*Ber.*, 21, 1572—1578).—Comparative fermentation experiments were made with galactose (very carefully purified) and dextrose, and the amount of alcohol formed in each case determined. In two experiments, the yeast was supplied with food, and in two experiments the yeast alone was employed. Galactose with food fermented more slowly but nearly as completely as dextrose. The percentages of alcohol were for galactose 45.15, for dextrose 45.59, instead of 51.11 per cent. When no food was supplied, the fermentation was incomplete after seven days, and only 11.13 and 16.60 per cent. of alcohol were obtained in each case.

In a second series of experiments, galactose and cane-sugar were fermented in presence of yeast-food, and cane-sugar with yeast alone. The same result was obtained with galactose as before, whilst the cane-sugar with yeast alone gave only 21.76 of alcohol instead of 53.80 per cent. (compare Pasteur, *Ann. Chim. Phys.* [3], 68, 337; Fudakowski, *Abstr.*, 1878, 776; v. Lippmann, *Abstr.*, 1885, 41; Kiliani, *Ber.*, 13, 1384; and Bourquelot, this vol., p. 573).

N. H. M.

Determination of the Molecular Weight of Raffinose and Formaldehyde by Raoult's Method. By B. TOLLENS and F. MAYER (*Ber.*, 21, 1566—1572).—In the following determinations, aqueous solutions were used: with raffinose the numbers 544, 594, 644, and 594 were obtained, which point to the formula $C_{18}H_{32}O_{16} + 5H_2O$ (compare de Vries, this vol., p. 667).

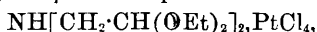
In the case of hexamethyleneamine, the numbers were 112 and 117. These numbers are in favour of the formula $C_6H_{12}N_4$ (140) rather than the formula $C_3H_6N_2$ (70) (compare Tollens, *Abstr.*, 1884, 988). Solutions of formaldehyde were prepared by heating oxymethylene with water at 130—150°. The following numbers were obtained: 35, 34, and 34, which show that formaldehyde has the formula CH_2O . The first two numbers were from preparations which had been kept for some days; the third preparation was examined after a few hours. The authors intend to apply the method to various carbohydrates.

N. H. M.

Acetalamine and Diacetalamine. By L. WOLFF (*Ber.*, 21, 1481—1484; compare *Abstr.*, 1887, 464, and also Wohl, this vol., p. 443).—Acetalamine and diacetalamine are produced when chloroacetal is heated at 130° with ammonia.

Acetalamine, $NH_2 \cdot CH_2 \cdot CH(OEt)_2$, remains in the solution when the product of reaction is shaken up with ether, and is separated by adding potassium carbonate and distilling. It is a colourless liquid, of disagreeable odour, which boils at 163°, and absorbs carbonic anhydride from the air. It is readily soluble in water, alcohol, ether, and chloroform, and is decomposed when left in contact with dilute acids. The strongly alkaline, aqueous solution, with mercuric chloride, gives a white, flocculent precipitate, and with auric chloride an oil which soon solidifies to yellow plates.

Diacetalamine, $NH[CH_2 \cdot CH(OEt)_2]_2$, is separated by fractioning the ethereal extract. It is a colourless liquid of disagreeable odour, which boils at 258—260° with slight decomposition. It is lighter than water, mixes in all proportions with alcohol, ether, and chloroform, and is decomposed by boiling with dilute sulphuric acid. When the strongly alkaline aqueous solution is heated, the base separates to a large extent in oily drops. The platinochloride,



crystallises in orange-red plates melting at 121°.

F. S. K.

Diazo-derivatives of Methyluracil. By R. BEHREND (*Annalen*, 245, 213—230).—*Diazo-isnitrosomethyluracil*, $C_5H_6N_4O_4$, is deposited on the addition of sodium nitrite (2 mols.) to a solution of crude amidomethyluracil in hydrochloric acid. On recrystallisation from

hot water, it is deposited in minute prisms. It is sparingly soluble in alcohol, but dissolves freely in alkalis, and is reprecipitated from alkaline solutions by acids. It is decomposed by prolonged boiling with water, or more easily by hydrochloric acid.

The nitro-derivative, $C_5H_4N_4(NO_2)O_4$, detonates at 100° . It expels carbonic anhydride from solutions of sodium carbonate. It is decomposed by warm water. Gas is evolved, and a substance of the composition $C_3H_2N_3O_2 + H_2O$ is deposited in crystals.

On reduction with stannous chloride and hydrochloric acid, diazoisoxanosomethyluracil yields hydroxylamine and isoxanthine, $C_5H_4N_4O_2$. Monobromisoxanthine, $C_5H_3BrN_2O_2 + H_2O$, crystallises in six-sided plates. At 150° it becomes anhydrous. W. C. W.

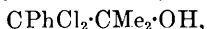
Cyanaldehyde. By P. CHAUTARD (*Compt. rend.*, **106**, 1167—1170).—170 grams of iodaldehyde dissolved in about twice its weight of absolute alcohol was mixed with 134 grams of dry powdered silver cyanide, and the mixture heated to boiling on a water-bath for 10 hours. The product was fractionated and dried over calcium chloride. The product is *cyanaldehyde*, a colourless, limpid, somewhat refractive liquid, with an odour recalling that of ethyl acetate. It is very volatile, and burns with a luminous but not smoky flame. It boils at 71.5° ; sp. gr. at $15^\circ = 0.881$; vapour-density, 2.33. It is miscible with water, and dissolves in all proportions in alcohol, ether, chloroform, and acetone. With sodium hydrogen sulphite, it forms a crystalline compound; it reduces Fehling's solution when heated, and is decomposed by soda, potash, and ammonia at a high temperature with formation of resinous products. Hydrochloric acid also yields resinous products, together with a small quantity of crystals. Boiling nitric acid converts cyanaldehyde into cyanacetic acid.

When heated with a large excess of aniline in sealed tubes at 300° for 16 hours, and the excess of aniline distilled off, cyanaldehyde yields crystals of *cyanethylenediphenyldiamine*, $CN \cdot CH_2 \cdot CH(NHPh)_2$, which melts at 113° .

Thiocyanaldehyde is obtained in a similar manner from iodaldehyde and silver thiocyanate. It is isomeric with acetyl thiocyanate, but is distinguished by its greater stability in presence of water. It is a very dense, viscid liquid with a fetid odour, and cannot be distilled without decomposition. C. H. B.

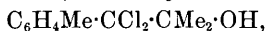
Acetonechloroform. By C. WILLGERODT and A. GENIESER (*J. pr. Chem.* [2], **37**, 361—374).—During the formation of solid acetonechloroform (Abstr., 1882, 491), a liquid isomeride is produced. This is best obtained when 300 to 350 grams of powdered potassium hydroxide is gradually added to a mixture of acetone (500 grams) and chloroform (1000 grams). The filtrate from the reaction is distilled, and the fraction 165 — 172° rectified. Liquid acetonechloroform boils at 170° (uncorr.), is a thick, colourless oil, stable in a sealed tube in the dark, but converted by light into a dark brown polymeride. It corrodes organic fabrics, and reddens blue litmus. In contact with water it is converted into the solid isomeride, which has no corrosive action, and is not so poisonous as the liquid; it also chars at a lower temperature.

Diphenylchloromethyl dimethyl carbinol, $\text{CPh}_2\text{Cl}\cdot\text{CMe}_2\cdot\text{OH}$, is obtained by heating a mixture of acetonechloroform, solid or liquid (1 mol.), with benzene (5 to 6 mols.), in presence of aluminium chloride (2 mols.) on the water-bath for 14 to 21 days, and subsequently distilling with steam. When redistilled it is a heavy, colourless oil, boiling about 239° (uncorr.). When less benzene is used in the reaction, *phenyldichloromethyl dimethyl carbinol*,



is obtained as colourless liquid, boiling about 217° ; and when an excess of benzene and a longer time are employed, *triphenylmethyl dimethyl carbinol*, $\text{CPh}_3\cdot\text{CMe}_2\cdot\text{OH}$, is formed; it is a pale-yellow liquid, boiling about 260° .

When toluene is substituted for benzene in these reactions, a mixture of *tolylchloromethyl dimethyl carbinol*,



and *ditolylchloromethyl dimethyl carbinol*, $\text{CCl}(\text{C}_6\text{H}_4\text{Me})_2\cdot\text{CMe}_2\cdot\text{OH}$, is obtained. The former is a bright yellow, heavy oil, boiling at 245° (uncorr.); the latter has a darker colour, and boils at 265° (uncorr.).

When paraxylene is used, the reaction takes place more readily, and *triparaxylylmethyldimethyl carbinol*, $\text{C}(\text{C}_6\text{H}_3\text{Me}_2)_3\cdot\text{CMe}_2\cdot\text{OH}$, is obtained; it is a bright greenish oil, and boils above 300° . These six condensation-products are all characterised by an odour of mushrooms.

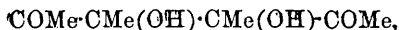
By treating liquid acetonechloroform with phosphorus pentachloride at 100° , carefully excluding all water, hydrogen chloride is evolved, and a clear colourless liquid may afterwards be distilled off. When washed and rectified, this boils at about 151° (uncorr.), and has the formula $\text{C}_4\text{H}_6\text{Cl}_2\text{O}$; it is insoluble in water, but soluble in organic solvents; its vapour strongly attacks the mucous membrane. When heated with dry silver oxide, oxygen is substituted for the chlorine; it is unchanged when heated with water at 240° . The behaviour of the solid isomeride with phosphorus pentachloride has been described before (Abstr., 1887, 570).

The structural formula which best expresses the above reactions of liquid acetonechloroform is $\text{CHCl}_2\cdot\text{CMe}_2\cdot\text{OCl}$. A. G. B.

α -Diketones. By H. V. PECHMANN (*Ber.*, **21**, 1411—1422).—The author has abandoned the sodium hydrogen sulphite method of preparing α -diketones (this vol., p. 248), and prefers to saponify the ethyl salt of methacetoacetic acid or its homologues with dilute (3 per cent.) alkali, to treat the product with sodium nitrite and sulphuric acid, and after removal of the alcohol by distillation to add 20 times its volume of dilute sulphuric acid (15 per cent.), and distil the mixture with steam (compare *loc. cit.*). The yield is not quite so good, but the method is more simple than that previously described.

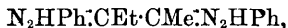
Diacetyl forms with alcohol an unstable compound, $\text{C}_4\text{H}_6\text{O}_2 + 2\text{C}_2\text{H}_6\text{O}$, which boils at $74\text{--}75^\circ$, and gives the reactions of diacetyl; it also slowly combines with water forming a crystalline compound, $3\text{C}_4\text{H}_6\text{O}_2 + 2\text{H}_2\text{O}$, insoluble in water, alcohol, and ether. The *phenylhydrazone*, $\text{COMe}\cdot\text{CMe}\cdot\text{N}_2\cdot\text{HPh}$, crystallises from dilute alcohol or acetic acid in lustrous, yellow needles, melts at 133° , and is soluble in

benzene and ether; the *diphenylhydrazone*, $N_2HPh \cdot CMe \cdot CMe \cdot N_2HPh$, crystallises from benzene in yellow needles, melts at 242° , and is very sparingly soluble in most solvents. When warmed with ortho-toluylenediamine acetate, diacetyl is converted into *dimethyltoluinoxaline*, $C_6H_3Me \langle \begin{smallmatrix} N \cdot CMe \\ N \cdot CMe \end{smallmatrix} \rangle$, which crystallises from light petroleum in hexagonal prisms, melts at 91° , boils at $270\text{--}271^\circ$ without decomposition, and is more soluble in cold than in hot water, and readily soluble in the ordinary solvents. Diacetyl also reacts with aniline, forming *diacetyldianil*, $NPh \cdot CMe \cdot CMe \cdot NPh$; this crystallises from alcohol in lustrous, sulphur-yellow scales, melts at 139° , and is readily soluble in ether, soluble in alcohol and light petroleum, but insoluble in water. When concentrated aqueous ammonia is added to an aqueous solution of diacetyl and the mixture after remaining some hours in the cold is heated at 100° for an hour, a mixture of bases is obtained, of which *trimethylglyoxaline*, $\langle \begin{smallmatrix} CMe \cdot N \\ CMe \cdot N \end{smallmatrix} \rangle CHMe$, constitutes the chief portion. This base crystallises from ether and light petroleum in bitter, snow-white needles, melts at $132\cdot5\text{--}133^\circ$, boils at 271° without decomposition, and is readily soluble in water and the ordinary solvents. It is a monacid base, and yields very soluble salts; the *hydrochloride*, $C_6H_{10}N_2 \cdot HCl$, crystallises in characteristic, snow-white tufts of needles. The base reacts readily with benzyl chloride and methyl iodide, but like other glyoxalines is not affected by nitrous acid. In aqueous solution acidified with dilute sulphuric acid, diacetyl is reduced by zinc-dust to the *pinacone*,



which crystallises from light petroleum in long, colourless needles, melts at 96° , is soluble in the ordinary solvents, reduces Fehling's solution in the cold, and is readily oxidised to diacetyl by ferric chloride and by mercuric chloride.

Acetylpropionyl, $COMe \cdot COEt$, prepared from ethylic ethacetoacetate by the method just described, is a dark yellow liquid, having a quinone-like odour, and boils at 108° with the formation of a yellow vapour. It dissolves in 15 parts of water at 15° , is readily soluble in the ordinary solvents, and forms an unstable compound with alcohol. The *phenylhydrazone*, $COEt \cdot CMe \cdot N_2HPh$, crystallises from dilute alcohol in yellowish, prismatic needles, melts at $96\text{--}98^\circ$, and is not identical with the acetylpropionyl hydrazone obtained by Japp and Klingemann by the action of diazobenzene chloride on ethylic ethacetoacetate (*Trans.*, 1888, 540); the *diphenylhydrazone*,



crystallises from alcohol in short, strongly refracting prisms, melts at $161\text{--}162\cdot5^\circ$, and is more soluble than the corresponding diacetyl-derivative. Acetylpropionyl reacts with aniline, forming a compound which crystallises in needles, and melts at $136\text{--}137^\circ$; it also yields a glyoxaline when treated with ammonia, but the compound could not be separated in a pure condition.

In forming these derivatives, diacetyl and its homologue resemble

glyoxal, benzil, and the other α -diketones, but they are differentiated from these on treatment with dilute aqueous alkali, inasmuch as they do not yield homologues of glycollic acid but are converted into triketones, and finally into quinones. *Dimethylquinogen*,



or its aldol, is obtained by carefully adding dilute aqueous soda or a dilute solution of sodium carbonate to an aqueous solution of diacetyl until it becomes colourless, when further action is at once prevented by acidification with dilute sulphuric acid, and the triketone extracted by ether. It is a yellowish syrup which does not solidify in the cold, has a bitter taste, and dissolves in the ordinary solvents. The *triphenylhydrazone*, $\text{C}_6\text{H}_{10}(\text{N}_2\text{HPh})_3$, is an orange-yellow crystalline powder consisting of tetragonal scales united in feather-like forms, and melts at $204-205^\circ$. Further treatment with an excess of alkali converts dimethylquinogen into paraxyloquinone. In like manner, acetylpropionyl is converted into the corresponding quinogen, which forms an oil sparingly soluble in water, and yields duroquinone (Nef, Abstr., 1886, 65) by the further action of aqueous soda. The quinone is obtained from the product by extraction with benzene at $70-80^\circ$, and crystallises from wood-spirit in long, golden-yellow needles melting at $111-112^\circ$; the yield amounts to about 10 per cent. of the diketone employed. The corresponding quinol crystallises from alcohol in lustrous needles, melts at 220° , and yields a phenylhydrazone which crystallises in white, spear-like forms, and melts at $223-225^\circ$.

W. P. W.

Action of Ethyl Chlorocarbonate on Salts of Fatty and Aromatic Acids. By R. OTTO and W. OTTO (*Ber.*, 21, 1516-1518; comp. Otto and Rössing, Abstr., 1885, 1231).—When sodium formate is warmed with ethyl chlorocarbonate in alcoholic solution, carbonic anhydride is evolved, and ethyl formate and formic acid are produced, together with sodium chloride and small quantities of diethyl carbonate. The quantity of formic acid produced is greater than that which would be liberated from the sodium salt by the hydrochloric acid which is formed by the action of the alcohol on the ethyl chlorocarbonate.

Sodium salts of higher members of the series behave similarly when treated with ethyl chlorocarbonate in presence of alcohol, and the more carbon the acid contains the larger the quantity of free acid produced, until finally (sodium stearate) no fatty ethereal salt is formed, but only the free acid (stearic), sodium chloride, and carbonic anhydride.

About 20 per cent. of formic acid is obtained from sodium formate, whilst sodium isovalerate yields about 50 per cent. of free acid.

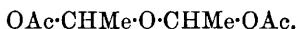
Equivalent quantities of sodium benzoate and ethyl chlorocarbonate in alcoholic solution yield ethyl benzoate and benzoic anhydride as principal products, besides sodium chloride, carbonic anhydride, and very small quantities of free benzoic acid.

Sodium phenylacetate and sodium oxalate also react with ethyl chlorocarbonate in presence of alcohol.

F. S. K.

Brominating Organic Acids. By C. HELL (*Ber.*, **21**, 1726—1729).—A reply to Volhard (this vol., p. 129).

Action of Ammonia on Ethylidene Oxyacetate. By A. GEUTHER (*Annalen*, **245**, 101—102).—Ammonia acts on ethylidene oxyacetate, forming acetamide, ammonium acetate, and aldehyde. The latter forms with ammonia the base $C_5H_{13}NO$, described by Wislicenus and Heintz (*Jahresbericht*, 1858, 347). The author represents the constitution of the oxyacetate by the formula



W. C. W.

Action of Iodoform, Methylene Iodide, and Iodine on Sodium Isobutyloxyde. By A. GORBOFF and A. KESSLER (*J. Russ. Chem. Soc.*, 1887, 428—463).—In 1858 Boutleroff showed that sodium ethoxide and iodoform yield methylene iodide, acrylic acid, and ethyllactic acids. It was expected by the authors, that iodoform with sodium isobutoxide would yield higher homologues of acrylic acid on the one hand, and of the ethoxypropionic acids on the other. Experiments made by the authors have shown that dimethacrylic acid, $C_5H_8O_2$, is formed in this reaction, as was expected, but the reaction is very complicated with regard both to the number and the character of the products formed. The yield of methylene iodide especially varied greatly, and as it has a disturbing action, it was necessary to conduct the reaction in such a way that its production was reduced to a minimum. Sodium isobutoxide was first prepared from 200 grams of isobutyl alcohol and 20 grams of sodium, and to this 100 grams of iodoform was added after a time. When the first violent reaction was over and the volatile portion (B) had distilled off, the residue (A) was extracted with water, the isobutyl alcohol removed by distillation, tartaric acid added, and the distillation continued. From the distillate containing the organic acids, the following were separated by fractional distillation: formic acid, and isobutyric acid; the portion boiling above 180° , when distilled under reduced pressure, yielded *dimethacrylic acid*, $CH_3CH_2CH(COOH)_2$, which was finally obtained in prismatic crystals melting at $69.5\text{--}70^\circ$, and boiling at $194\text{--}195^\circ$, sublimation taking place at a lower temperature. Ten degrees above the boiling point, the acid decomposes into isobutylene and carbonic anhydride. The monoclinic dibromide melts at $107\text{--}108^\circ$. From the higher boiling portions, besides dimethacrylic acid, α -isobutoxyisobutyric acid, $C_4H_8O \cdot CH_3CH_2CH(COOH)_2$, was obtained.

The oily portion from A was mixed with the oily portion obtained from the higher boiling acids, and distilled under reduced pressure, when an aromatic neutral liquid was obtained of the composition $C_8H_{14}O_2$, and having the properties of an octolactone. This the authors consider to be isomeric with the octolactones of Young and of Emmert and Friedrich. The portion B has an ethereal odour, and contains, besides isobutyl alcohol, isobutylene, methyl isobutyl ether, and diisobutyl methylene ether, a compound of the composition $C_{12}H_{26}O_3$, and a mixture of substances which could not be separated by fractional distillation under reduced pressure. The compound

$C_{12}H_{26}O_3$ yielded isobutyl iodide when heated with hydriodic acid, showing that it contains isobutoxyl groups, and with acetic acid α -hydroxyisobutaldehyde was obtained as a product of decomposition, together with isobutyl acetate; of the last, according to quantitative experiments, 2 mols. are formed, and the authors therefore consider the compound $C_{12}H_{26}O_3$ to be the isobutyl alcoholate of α -isobutoxyisobutaldehyde, $C_4H_9 \cdot O \cdot CMe_2 \cdot CH(OH) \cdot O \cdot C_4H_9$, which, as quantitative experiments show, decomposes into, $C_4H_{10}O$ and $C_4H_9 \cdot O \cdot CMe_2 \cdot COH$. Of the products obtained in this reaction, the following are derived from the iodoform: acetic and dimethacrylic acids, methyl isobutyl ether and diisobutyl methylene ether. In the case of the formation of isobutyric and isobutyl- α -hydroxyisobutyric acids, of the octolactone and of the compound $C_{12}H_{26}O_3$, the carbon-atom of iodoform could not have taken any part, as they contain a number of carbon-atoms which corresponds with single or multiple isobutylic groups. No isobutyl orthoformate is formed, as might have been expected, for iodoform acts on isobutyl alcohol in such a way that, in the first place, reduction of the iodoform to methylene diiodide takes place, which with sodium isobutoxide yields diisobutyl methylene ether, and then a further reduction to methyl iodide which with an excess of the alkoxide yields methyl isobutyl ether. Direct experiments have shown that the said ethers, together with isobutyric acid and the octolactone, are obtained when sodium isobutoxide acts on methylene diiodide. The hydrogen which had reduced the triiodide to the diiodide and moniodide, must have been taken from the alcohol, just as in the experiments of Bolas and Groves on carbon tetrabromide, which with alcohol yielded bromoform together with aldehyde and hydrogen bromide. The authors give a theoretical explanation of the formation of the compound $C_{12}H_{26}O_3$.

On acting with free iodine on sodium isobutoxide, the compound $C_{12}H_{26}O_3$ was obtained, together with octolactone and α -isobutoxyisobutyric acid. It seems that by acting with iodine (and bromine) on the metallic derivatives of other monatomic alcohols, substances analogous to those obtained above are formed in some cases. The authors propose to investigate this matter.

B. B.

Isoleïc Acid. By M. C. and A. SAYTZEFF (*J. pr. Chem.* [2] **37**, 269—290; compare *Abstr.*, 1887, 30).—When iodostearic acid, obtained by the action of hydriodic acid on ordinary oleïc acid, is heated in a reflux apparatus with alcoholic potash, and the product of the reaction is decomposed with sulphuric acid, together with ordinary oleïc acid, an isomeride is formed which melts and solidifies at 44—45°. This solid oleïc acid may be also prepared by distilling hydroxystearic acid, obtained by the successive action of sulphuric acid and water on ordinary oleïc acid. The best yield is obtained if the operation is conducted under a pressure of 100 to 150 mm., when the distillation takes place at 280—300°. Oleïc and isoleïc acids can be separated by means of their zinc salts, that of the latter being less soluble in alcohol.

Isoleïc acid, $C_{18}H_{34}O_2$, is insoluble in water, dissolves readily in alcohol and ether, and forms a liquid dibromide, $C_{18}H_{34}O_2Br_2$, isomeric

with that obtained from oleic acid, but differing from it in not reacting in the cold with silver oxide. It furnishes a *dihydroxystearic acid* which differs from its isomeride, not only in its melting point ($76-78^{\circ}$) and solidifying point ($66-64^{\circ}$), but also in being much more soluble in alcohol and ether. This new dihydroxystearic acid on treatment first with hydriodic acid, and then with tin and hydrochloric acid, gives ordinary stearic acid.

Isoleic acid combines with hydriodic acid to form a new iodostearic acid. This is a thick yellow oil, and differs from its isomeride in not readily reacting with silver oxide, in being more soluble in alcohol and ether, and in undergoing no change on distillation.

Iodostearic acid, prepared from isoleic acid, gives only isoleic acid when boiled with alcoholic potash, whilst that formed from ordinary oleic acid gives a mixture of oleic and isoleic acids. When fused with potash, isoleic acid behaves like its isomerides, and gives a mixture of palmitic and acetic acids. When oxidised with permanganate in alkaline solution, isoleic acid yields a mixture of dihydroxystearic acid and a saturated bibasic acid not yet investigated.

Two hydroxystearic acids are formed when isoleic acid is treated first with sulphuric acid and then with water. Of these, one is identical with that prepared from the iodostearic acid derived from ordinary oleic acid, the other with that derived from the iodostearic acid prepared from isoleic acid. The behaviour of the two isomerides leads the authors to give the formula $\text{CH}_3[\text{CH}_2]_{13}\text{CH}_2\text{CH}:\text{CH}\cdot\text{COOH}$, to isoleic acid, ordinary oleic acid being represented by the formula $\text{CH}_3[\text{CH}_2]_{13}\text{CH}:\text{CH}\cdot\text{CH}_2\text{COOH}$.
G. T. M.

Acids from Drying Oils. By K. HAZURA (*Monatsh.*, **9**, 180—197; compare Abstr., 1887, 359, 798, 913).—*Isolinusic acid* (15.8 per cent.), and dihydroxystearic acid (1.2 per cent.) are obtained together with sativic acid (6.5 per cent.) and linusic acid (4.5 per cent.) when linoleic acid is oxidised with alkaline potassium permanganate (Abstr., 1887, 798).

Isolinusic acid, $\text{C}_{18}\text{H}_{36}\text{O}_8$, crystallises in small, anhydrous, prismatic needles which melt at $173-175^{\circ}$, are insoluble in ether, benzene, toluene, carbon bisulphide and chloroform, sparingly soluble in cold water and cold alcohol, but readily soluble in hot water or hot alcohol. *Acetylisolinusic acid* has the same properties as acetyllinusic, but it is more sparingly soluble in ether. The analysis of this acetyl-derivative showed that six hydroxyl-groups and one carboxyl-group are present in isolinusic acid, the formation of which from the liquid fatty acid of linseed oil necessitates the assumption that the glyceride of an acid, $\text{C}_{18}\text{H}_{30}\text{O}_2$, isomeric with linolenic acid, is also present in linseed oil. The author names this acid *isolinolenic acid*.

The alkaline salts of isolinusic acid are very readily soluble in water; the *potassium* and *sodium* salts crystallise from water in microscopic needles. The *barium* salt crystallises from hot water in microscopic needles. The *calcium* salt is soluble in hot water. Copper sulphate produces a green, silver nitrate, a white precipitate in an aqueous solution of the alkaline salts; both precipitates are insoluble in water.

Sativic acid crystallises either in long, prismatic, microscopic needles, or in pyramidal prisms according to the purity and concentration of the solution. It melts at 173° .

Linusic acid (Abstr., 1887, 798), crystallises from dilute aqueous solutions in needles, but from concentrated solutions in rhombic plates, the opposite ends of which are often blunt. When sativic acid is treated with nascent hydrogen iodide, a thick, brownish, oily iodo-compound is obtained, and this oil is converted into stearic acid by nascent hydrogen. Sativic acid is therefore tetrahydroxystearic acid.

From the regular behaviour of alkaline solutions of unsaturated fatty acids towards potassium permanganate (Abstr., 1887, 913), it follows that the liquid fatty acid from linseed oil consists of oleic acid, linoleic acid, linolenic acid, and isolinolenic acid.

Oleic acid dibromide, linoleic acid tetrabromide, linolenic acid hexabromide, and isolinolenic acid hexabromide, are formed when linoleic acid is treated with bromine.

F. S. K.

Acids from Drying Oils. By K. HAZURA and A. GRÜSSNER (*Monatsh.*, 9, 198—207).—From the author's experiments, based on the regular behaviour of unsaturated fatty acids towards alkaline permanganate (Abstr., 1887, 913), it follows that the fatty acids from hemp-seed oil, poppy oil, nut oil, and cotton-seed oil, are not homogeneous compounds, but mixtures of unsaturated acids.

The fatty acids from hemp-seed and nut oil consist chiefly of linoleic acid, together with small quantities of linolenic, isolinolenic, (compare preceding Abstract), and oleic acid.

The fatty acid from poppy oil consists chiefly of linoleic acid, together with considerable quantities of oleic acid, and very small quantities of linolenic and isolinolenic acids.

The fatty acid from cotton-seed oil contains only linoleic acid and oleic acid.

The method employed in determining the constitution of the fatty acid was, in all cases, the following:—It is oxidised with alkaline potassium permanganate, the product (A + B) precipitated with sulphuric acid, dried, and treated with cold ether; the dihydroxystearic acid (A) dissolves, and the residue (B) is boiled out with water to separate the sativic acid from any dihydroxystearic acid which had not been dissolved by the ether. The acids thus separated were recognised by the usual means. The filtrate from the mixture (A + B) is neutralised with soda, evaporated, again precipitated with sulphuric acid, and the precipitate extracted with ether; the residue is recrystallised from alcohol or water, and the acid mixture (linusic and isolinusic acids) examined microscopically. In the case of cotton-seed oil, the precipitate, which probably contained azelaic acid only, was completely soluble in ether.

F. S. K.

Halogen Substitution Products of Ethyl Acetoacetate and their Behaviour with Sodium Ethoxide. By W. MEWES (*Annalen*, 245, 58—84).—Ethyl dichloroacetoacetate is formed by

saturating ethyl acetoacetate with chlorine in diffused daylight. If the product is treated with chlorine in direct sunlight, the trichloro- and tetrachloro-derivatives are formed.

Chlorobromo-substitution products are obtained by the action of bromine on the chloro-substitution products, and also by the action of chlorine on the bromo-derivatives.

Sodium ethoxide decomposes ethyl chloracetoacetate, forming ethyl acetate and chloracetate. Ethyl dichloracetoacetate is split up into ethyl acetate and dichloracetate. The chief product of the action of sodium ethoxide on ethyl trichloracetoacetate is ethyl dichloracetate. Ethyl acetate and chloracetate are also formed in small quantity. Under similar treatment, ethyl tetrachloracetoacetate yields ethyl acetate, chloracetate, and dichloracetate.

Ethyl bromacetoacetate gives a good yield of ethyl succinosuccinate, when it is treated with sodium ethoxide. The author confirms Wedel's statement (Abstr., 1884, 434) that the chief product of the action of sodium ethoxide on ethyl dibromacetoacetate is ethyl quinonehydridicarboxylate. When the chlorobromo-substitution products of ethyl acetoacetate are treated with sodium ethoxide, sodium bromide is invariably formed; thus ethyl monochlorodibromacetoacetate yields ethyl chlorobromacetate. W. C. W.

Homologues of Ethyl Acetocyanacetate. By A. HALLER (*Compt. rend.*, 106, 1083—1085).—The homologues of ethyl acetocyanacetate are obtained by the action of the corresponding acid chlorides on ethyl sodiocyanacetate. 22.6 grams of ethyl cyanacetate dissolved in 30 grams of absolute alcohol is mixed with a solution of 4.6 grams of sodium in 100 parts of absolute alcohol, and the theoretical quantity of the acid chloride, diluted with four or five times its volume of ether, is added gradually to the well-cooled mixture. The product is isolated in the manner previously described (Abstr., 1887, 1029).

The compounds thus obtained are colourless, strongly acid liquids, with an odour resembling both that of the ethyl cyanacetate and that of the corresponding acid. Their salts are usually soluble in alcohol, from which they often separate in viscous masses which will not crystallise. They can, however, be obtained in crystals by dissolving them in dilute alcohol and evaporating spontaneously over sulphuric acid.

Ethyl propiocyanacetate, $\text{CH}_2\text{Me}\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{COOEt}$, boils at 155—165°, under a pressure of 50 mm. The calcium salt crystallises in long needles, which contain 2 mols. H_2O , and are very soluble in water and alcohol.

Ethyl butyrocyanacetate, $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{COOEt}$, boils at 166—178° under a pressure of 66 mm. The calcium salt forms crystalline crusts which contain 2 mols. H_2O ; the barium salt crystallises in nacreous mamelons which contain 3.5 mols. H_2O . The ferric salt is a viscous, non-crystalline, deep-red compound, soluble in ether.

Ethyl isobutyrocyanacetate, $\text{CHMe}_2\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{COOEt}$, boils at 170—177°, under a pressure of 85 mm. The calcium salt forms

distinct crystals which contain 2 mols. H_2O and are slightly soluble in water, and soluble in alcohol. C. H. B.

Action of Acetic Anhydride on Levulinic Acid. By G. MAGNANINI (*Ber.*, **21**, 1523—1524).—An acid, $\text{C}_9\text{H}_{10}\text{O}_4$, is obtained by heating levulinic acid at $200\text{--}225^\circ$ with acetic anhydride. It crystallises from boiling water in small needles melting at $151.5\text{--}152^\circ$. The silver salt, $\text{C}_9\text{H}_9\text{O}_4\text{Ag}$, is a crystalline compound, which is sparingly soluble in water and remains unchanged on exposure to the air. The barium salt, $(\text{C}_9\text{H}_9\text{O}_4)_2\text{Ba} + \text{H}_2\text{O}$, is also crystalline. F. S. K.

Methyl Propiopropionate. By C. PINGEL (*Annalen*, **245**, 84—95).—Methyl propiopropionate boils at 187° (corr.), and its sp. gr. at 20° is 1.070. It is converted into a mixture of an oily and a crystalline amide by treatment with strong ammonia. The oily liquid has the composition $\text{C}_7\text{H}_{13}\text{NO}_2$, and the crystalline amide is probably $\text{C}_7\text{H}_{13}\text{NO}_2 + \text{C}_3\text{H}_9\text{NO}_2$. Diethyl ketone and methyl ethyl ketone are formed by the action of sodium hydroxide on methyl propiopropionate.

Methyl methylpropiopropionate and methyl ethylpropiopropionate are respectively formed by the action of methyl or ethyl iodide on methyl propiopropionate and sodium ethoxide in sealed tubes at 100° . The methyl salts of methylpropiopropionic, ethylpropiopropionic, propylpropiopropionic, and isobutylpropiopropionic acids boil at $193\text{--}196^\circ$, 208° , $217\text{--}221^\circ$, and $230\text{--}231^\circ$ respectively. W. C. W.

New Synthesis of Dihydric Monobasic Acids from Ketones. By S. REFORMATSKY (*J. Russ. Chem. Soc.*, 1887, 298—299).—By the action of zinc and allyl iodide on ethyl chloracetate a compound is obtained which contains oxygen, is neutral and unsaturated, and decomposes on distillation. It is insoluble in water, and very stable, not being decomposed by alkalis or acids. It has not the properties of an alcohol. It would seem that it is formed by the mutual reaction of 2 molecules of ethyl chloracetate in the presence of zinc. Acetone with ethyl chloracetate and zinc, or better, ethyl iodacetate and zinc, yields β -dimethylethylenelactic (hydroxyvaleric) acid. The research is being continued. B. B.

Action of Aniline on Isosaccharin. By B. SOROKIN (*J. pr. Chem.* [2], **37**, 318—320).—When aniline (3 parts) is heated to the boiling point with isosaccharin (1 part) in an oil-bath, and ether is added to the product, a substance of a brownish colour is precipitated, which on crystallisation from alcohol forms colourless needles, having the formula $\text{C}_{12}\text{H}_{17}\text{NO}_8$, and melting at 165° without decomposition. This substance, which is formed by the direct union of 1 mol. of aniline with 1 mol. of isosaccharin, without elimination of water, is readily dissolved by alcohol and water, but the solution is levorotatory. An aqueous solution is slightly acid; it does not, however, decompose calcium carbonate, but on treatment with lime-water forms calcium isosaccharinate, $(\text{C}_6\text{H}_{11}\text{O}_8)_2\text{Ca}$, and aniline. The substance is an anilide of isosaccharinic acid of the formula $\text{C}_6\text{H}_{11}\text{O}_4\cdot\text{CO}\cdot\text{NHPh}$, and

like the anilides of other acids readily splits up into its components on treatment with acids and alkalis.

G. T. M.

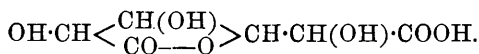
Preparation of Dibromosuccinic Acid. By J. GORODETZKY and C. HELL (*Ber.*, 21, 1729—1733).—Dibromosuccinic acid is best prepared by heating a mixture of 30 grams of dry succinic acid, 0.15 gram of amorphous phosphorous, and 21 c.c. of dry bromine, in three equal parts in sealed tubes at 120—130° for about six hours. 46 gram of dibromosuccinic acid, 12.5 grams of monobromosuccinic acid, and 2.5 grams of unchanged succinic acid are thus obtained. The product is well rubbed several times with lukewarm water, and the residual dibromosuccinic acid crystallised quickly from boiling water. When the temperature is quickly raised to 140°, and then lowered gradually to 130—120°, the risk of bursting the tubes is considerably lessened.

F. S. K.

Action of Ethyl Iodide and Zinc, and of Allyl Iodide and Zinc on Ethereal Malonates. By B. MARTINOFF and S. SHUKOFFSKY (*J. Russ. Chem. Soc.*, 1887, 297—298).—In the first reaction, ethereal salts of diethylmalonic acid are formed, and in the second corresponding salts of diallylmalonic acid. Hydrocarbons are produced at the same time.

B. B.

Crystallised Saccharic Acid. By O. SOHST and B. TOLLENS (*Annalen*, 245, 1—27).—Saccharic acid is best prepared by adding 100 grams of powdered potato-starch suspended in 100 c.c. of water to 500 c.c. of nitric acid, sp. gr. 1.15. The mixture is heated at 60—70° until the evolution of red fumes almost ceases, and the product is then diluted with an equal volume of water and the warm liquid neutralised by potassium carbonate. On the addition of strong acetic acid, the acid potassium salt, $C_6H_8O_8K$, is deposited in microscopic crystals. This salt is converted into silver saccharate by double decomposition, and the free acid is obtained by acting on the silver salt with hydrochloric acid. On leaving the concentrated solution for some days in an atmosphere free from ammonia, crystals of saccharic acid are deposited. After drying on porous plates at the ordinary temperature, the crystals have the composition $C_6H_8O_7$, the anhydride of saccharic acid. At the ordinary temperature, saccharic acid is monobasic, but the hot aqueous solution neutralises two equivalents of alkali. Saccharic acid behaves like a lactonic acid. Its constitution is probably



The specific rotation of a freshly prepared aqueous solution of the crystallised acid is +37.6—37.9°, but after a time it steadily diminishes to +18.9—22.5°. On the other hand, a solution prepared by the addition of hydrochloric acid to the ammonium salt only exhibits a rotatory power of +8.4—9.3°, which rises to +22.66° in course of time. The saccharates of ammonium, $C_6H_8O_8 \cdot NH_4$, and magnesium, $C_6H_8O_8 Mg + 3H_2O$, are crystalline. Barium forms two normal

saccharates, an anhydrous crystalline salt, and an amorphous salt containing $2\frac{3}{4}$ or 3 mols. H_2O . At 150° , saccharic acid is decomposed by strong hydrochloric acid, yielding dihydromucic acid.

W. C. W.

Metasaccharic Acid. By H. KILIANI (*Ber.*, 21, 1422—1424).—Maquenne (this vol., p. 677) has recently stated that the diphenylhydrazone of saccharic acid melts at the same temperature and has properties similar to those of the diphenylhydrazone of metasaccharic acid (*ibid.*, p. 46), and has suggested that the two acids may be identical. The author, however, points out that the diamides of the two acids are not identical, and that potassium metasaccharate, unlike the saccharate, does not yield the potassium hydrogen salt on treatment with acetic acid. Dextrose and gluconic acid, when oxidised under the same conditions as arabinosecarboxylic acid, are not converted into the double lactone of metasaccharic acid, and it was not found possible to obtain saccharic acid by heating the double lactone with water, as the latter almost completely decomposed.

W. P. W.

Alkyl Salts of Sulphoacetic Acid and Ethyldenedisulphonic Acid. By R. MAUZELIUS (*Ber.*, 21, 1550—1552).—*Diethylsulphoacetate*, $\text{SO}_3\text{Et}\cdot\text{CH}_2\cdot\text{COOEt}$, is prepared by the action of ethyl iodide on the silver sulphonate of ethyl acetate. The product is extracted with ether and dried with calcium chloride; on distilling off the ether, a yellowish liquid is obtained which can be made colourless by heating it in a beaker. It does not distil without decomposition.

Diethyl ethyldenedisulphonate, $\text{CHMe}(\text{SO}_3\text{Et})_2$, is formed when the corresponding silver salt is gently heated with ethyl iodide. It is a slightly red oil of peculiar odour, readily soluble in alcohol and ether, insoluble in aqueous soda and in water. It decomposes readily when heated. The *silver salt*, $\text{CHMe}(\text{SO}_3\text{Ag})_2 + \text{H}_2\text{O}$, crystallises in slender needles. The *sodium-derivative*, $\text{CMeNa}(\text{SO}_3\text{Et})_2$, prepared by the action of sodium ethoxide on the ethyl salt, forms globular groups of small needles.

Butanedisulphonic acid, $\text{CMeEt}(\text{SO}_3\text{H})_2$, is formed when the above sodium-derivative is boiled with alcohol and ethyl iodide in a reflux apparatus. The product is dissolved in water and neutralised, when the *sodium salt* separates in long, flat needles, very readily soluble in water.

N. H. M.

Action of Iodobenzene on Silver Nitrite. By A. GEUTHER (*Annalen*, 245, 99—101).—Silver nitrite does not act on iodobenzene at a temperature below 135° , but between 140° and 150° a reaction takes place resulting in the formation of trinitrophenol, silver iodide, and metallic silver.

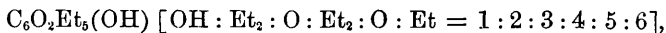
W. C. W.

Additive Product of Tribromodinitrobenzene and Tetrabromodinitrobenzene. By C. L. JACKSON and G. D. MOORE (*Ber.*, 21, 1707—1708).—An additive product, $2\text{C}_6\text{HBr}_3(\text{NO}_2)_2\cdot\text{C}_6\text{Br}_4(\text{NO}_2)_2$, is formed when tribromodinitrobenzene (2 mols.) and tetrabromodinitrobenzene (1 mol.) are mixed together in benzene solution. It crystallises from alcohol in rhombic leaves melting at 165° , which are

tolerably stable and can be recrystallised from ordinary solvents, but are partially decomposed by methyl alcohol or by a mixture of methyl and ethyl alcohol.

F. S. K.

Desmotropy in Phenols. Bissecondary Pentethylphloroglucinol. By J. HERZIG and S. ZEISEL (*Monatsh.*, 9, 217—226).—*Pentethylphloroglucinol*,



is prepared as follows: phloroglucinol (1 mol.) is mixed with potash (3 mols.), dissolved in lukewarm 25 per cent. alcohol, and ethyl iodide (3 mols.) added. After the first somewhat energetic reaction ceases, the mixture is warmed for two hours, the alcohol distilled off, and the residue dissolved in water and extracted with ether. The ethereal solution is then shaken with potash until the latter is no longer coloured yellow, and on evaporating the ether a yellow, indifferent oil (Benedikt, this Journal, 1876, i, 250; Will and Albrecht, *Abstr.*, 1884, 1335) remains. The potash is neutralised with hydrochloric acid with addition of a little sodium sulphite, and extracted with ether; when the ether is distilled, a brown product remains which is again treated with potash and ethyl iodide as described above, and the products separated as before. A yellow, indifferent oil and a compound which is soluble in potash are again obtained. The potash solution is acidified, extracted with ether, and the ether distilled, when the greater part of the residual pentethylphloroglucinol quickly solidifies. It crystallises from alcohol in white plates melting at 91—94°, but when the alcohol is too dilute, it separates in an oily condition and then solidifies to leafy crystals. It is not acted on when boiled with hydrogen iodide for two hours, and neither this compound nor the indifferent oil shows the pinewood reaction of phloroglucinol.

Hexethylphloroglucinol, $\text{C}_6\text{O}_3\text{Et}_6$, is obtained by treating the penta-derivative with potash and ethyl iodide, but even with a large excess of the reagents a considerable quantity of pentethylphloroglucinol remains unchanged. It is an oily compound and completely insoluble in potash. One ethyl-group is readily and quantitatively eliminated as ethyl iodide, when it is treated with hydrogen iodide according to Zeisel's method.

The indifferent oil alluded to above is probably a mixture of the ethyl-derivatives of various pseudo-forms of phloroglucinol.

F. S. K.

Preparation of Nitramines from Nitrophenols. By A. BARR (*Ber.*, 21, 1541—1549).—Merz and Ris (*Abstr.*, 1886, 872) obtained ortho- and para-nitraniline by heating the corresponding nitrophenols with aqueous ammonia. In a similar manner Witt (*Abstr.*, 1886, 947) prepared dinitronaphthylamine from α -dinitronaphthol.

Dinitraniline, $[\text{NH}_2 : (\text{NO}_2)_2 = 1 : 2 : 4]$, is obtained by heating 3 grams of dinitrophenol (m. p. 112°) with 10 c.c. of 27 per cent. ammonia for 16 hours at 175°; the product is filtered and the red needles shaken with water containing ammonia and ether. The ethereal solution is separated, dried, and the ether distilled off. It

crystallises in light-yellow crystals melting at 176° (not 182°). The yield is 60 per cent. of the weight of dinitrophenol.

Metanitroparatoluidine is prepared by heating 3 grams of pure nitroresol with 8 c.c. of 35 per cent. ammonia for 16 hours at $170-180^{\circ}$. The yield is 63 per cent. of the weight of the nitroresol.

Dinitrotoluidine, $[\text{Me} : \text{NH}_2 : (\text{NO}_2)_2 = 1 : 2 : 3 : 5]$, is formed when 3 grams of dinitroresol is heated with 10 c.c. of 27 per cent. ammonia for 20 hours at $175-185^{\circ}$. It crystallises from xylene in yellow prisms melting at 208° .

Dinitroisobutylaniline, $\text{NH}_2 \cdot \text{C}_6\text{H}_2(\text{C}_2\text{H}_5)(\text{NO}_2)_2$, prepared by heating 3 grams of the dinitrophenol with 10 c.c. of 27 per cent. ammonia for 15 hours at 175° , crystallises from warm alcohol in slightly yellowish-brown, feathery crystals melting at 127° . It sublimes in yellow needles, is readily soluble in ether and warm alcohol, insoluble in boiling water.

Dinitrophenylenediamine, $[\text{NH}_2 : \text{NO}_2 : \text{NH}_2 : \text{NO}_2 = 1 : 2 : 3 : 4]$, is obtained when 4 grams of dinitroresorcinol is heated with 15 c.c. of 27 per cent. ammonia for 20 hours at 115° . It crystallises from glacial acetic acid in groups of light yellowish-brown needles which melt with decomposition at about 250° . It is very sparingly soluble in alcohol, ether, and benzene. The isomeric dinitro-amido-compound described by Nietzki and Hagenbach melts at about 300° (Abstr., 1887, 477).

Trinitrophenylenediamine, $\text{C}_6\text{H}_3\text{N}_4\text{O}_6$, obtained by boiling diethyl-trinitroresorcinol with alcoholic ammonia for a short time, separates from its solution in glacial acetic acid in crystalline grains which do not melt at 250° , and detonate slightly when heated in a flame. It is almost insoluble in the usual solvents except glacial acetic acid. Boiling aqueous sodium carbonate decomposes it with liberation of ammonia. When reduced with tin and strong hydrochloric acid, *pentamidobenzene hydrochloride*, $\text{C}_6\text{H}(\text{NH}_2)_5\text{HCl}$, is formed. This crystallises in hair-like needles, very readily soluble in cold water, almost insoluble in alcohol and ether. When the aqueous solution is exposed to air, it becomes violet and a dark substance separates. The free base was not isolated. The *pentacetyl-derivative*, $\text{C}_6\text{H}(\text{NHAc})_5$, forms an almost insoluble, amorphous powder. Pentamidobenzene reacts without difficulty with benzaldehyde, phenanthraquinone, and benzil, &c., with formation of crystalline compounds.

Trinitrophenylenediamine could not be prepared from trinitroresorcinol and ammonia.

N. H. M.

Cyanacetates of the Benzene Series. By A. HALLER (*Compt. rend.*, 106, 1171—1174).—An aqueous solution of sodium nitrite containing 1 gram-molecule per litre, and a solution containing 1 gram-molecule of aniline and 3 gram-molecules of hydrochloric acid per litre are prepared, and likewise hydrochloric acid solutions of orthotoluidine and paratoluidine half the strength of the aniline solution.

100 c.c. of the aniline solution or 200 c.c. of toluidine solution is cooled at 0° and mixed with 100 c.c. of the nitrite solution and a solution of ethyl sodiocyanacetate obtained by treating 11.3 grams of

ethyl cyanacetate in 50 grams of ethyl alcohol with 2·3 grams of sodium dissolved in 50 grams of alcohol. If methyl-derivatives are required, 9·9 grams of methyl cyanacetate in 30 grams of methyl alcohol is substituted for the ethyl cyanacetate and sodium methoxide for the ethoxide. The product separates as a yellow precipitate which is dissolved in potash, precipitated with sulphuric acid, washed with water, dried, and recrystallised from alcohol.

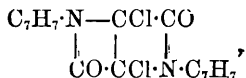
The derivatives thus obtained are yellow crystalline compounds insoluble in water, slightly soluble in cold alcohol, soluble in hot alcohol and in benzene, chloroform, ether, and alkalis. They also dissolve in hot solutions of alkaline carbonates.

Methyl azobenzenecyanacetate forms slender needles which melt at 86·5°. The corresponding ethyl salt melts at 124·9°. *Methyl azotoluencyanacetate* [1 : 2] forms silky needles which melt at 167·2°. The ethyl salt melts at 125·8°. *Methyl azotoluenecyanacetate* [1 : 4] melts at 133·5°, and the ethyl salt at 74·4°.

The solubility in alkalis indicates that these compounds have the constitution $R \cdot N_2 \cdot CH(CN) \cdot COOR$, and not $R \cdot NH \cdot N \cdot C(CN) \cdot COOR$, and the solubility in alkaline carbonates shows that the introduction of N_2 into the CH_2 -group of the cyanacetates has greatly increased the activity of the acid function.

C. H. B.

Bromacetorthotoluide and some of its Derivatives. By P. W. ABENIUS and O. WILDMAN (*Ber.*, 21, 1662—1664).—*Bromacetorthotoluide*, prepared by the action of bromacetic bromide on orthotoluidine dissolved in benzene, crystallises in white needles melting at 113°. When this compound or the chlorinated derivative (m. p. 111—112°) is boiled with aqueous potash, *diorthotolyldiketopiperazine*, $C_6H_4Me \cdot N < \begin{smallmatrix} CO \cdot CH_2 \\ CH_2 \cdot CO \end{smallmatrix} > N \cdot C_6H_4Me$, is obtained. This crystallises in well-formed plates which melt at 159—169°, is insoluble in bases and in dilute acids. The platinochloride (with 4 mols. H_2O) melts at 176°. When boiled with an excess of alcoholic potash for half an hour, *orthotolylglycinyorthotolyglycine* (*orthotolylglycinorthotolyamidacetic acid*), $C_7H_7 \cdot NH \cdot CH_2 \cdot CO \cdot N(C_7H_7) \cdot CH_2 \cdot COOH$, is formed; this melts at 129°. Phosphorus pentachloride reacts with ditolyldiketopiperazine at 140° with formation of the compound



which crystallises in slender needles melting at 200—201°.

Chloracetylorthotolyglycine, $C_6H_4Me \cdot N(CO \cdot CH_2Cl) \cdot CH_2 \cdot COOH$, is prepared by mixing ethereal solutions of chloracetyl chloride and orthotolyglycine; it crystallises from benzene in well-formed plates and melts at 116—117°; when heated with 2 mols. orthotoluidine at 160°, it is converted into diorthotolyldiketopiperazine.

Tetrabromodiorthotolyldiketopiperazine, $C_{18}H_{14}Br_4O_2$, is obtained by brominating orthacetotoluide at 160° and boiling the orthobromacetodibromotoluide so formed with alcoholic potash. It crystallises in plates and melts at 277°.

N. H. M.

Lactones derived from Glycines. By P. W. ABENIUS (*Ber.*, 21, 1668—1669).—*Glycolylorthotolylglycin*,



is formed when chloracetylorthotolylglycin (preceding Abstract) is boiled with an excess of soda. It crystallises in hexagonal leaves or prisms which melt at 143—144°, are readily soluble in water, alcohol, ether, chloroform, acetone, &c., but tolerably sparingly soluble in benzene.

Anhydroglycolylorthotolylglycin, $\text{C}_7\text{H}_7\cdot\text{N}<\begin{smallmatrix} \text{CH}_2\cdot\text{CO} \\ \text{CO}\cdot\text{CH}_2 \end{smallmatrix}>\text{O}$, is obtained by heating the preceding compound at 160°. It crystallises from alcohol, in which it is readily soluble, in long prisms melting at 108—109°. It behaves like a lactone, dissolves slowly in cold caustic alkalis and in warm alkaline carbonates with regeneration of glycolyl-orthotolylglycin. F. S. K.

Pentamidobenzene. By A. W. PALMER and C. L. JACKSON (*Ber.*, 21, 1706—1707).—Triamidodinitrobenzene, prepared from tribromodinitrobenzene melting at 192°, is an amorphous, yellow compound. It yields a colourless reduction product, the hydrochloride of which, $\text{C}_6\text{H}(\text{NH}_2)_2(\text{NH}_3\text{Cl})_3$ or $\text{C}_6\text{H}(\text{NH})_2(\text{NH}_3\text{Cl})_3$, is a white powder which gradually turns brown on exposure to the air. F. S. K.

Orthazotoluene. By W. POSPECHOFF (*J. Russ. Chem. Soc.*, 1887, 402—413).—According to Werigo and Petrieff this compound melts at 137°. The “ortho-azotoluene” of Hoogewerff and van Dorp melts at 55°, and is different from Petrieff’s. Kissel, on repeating Hoogewerff and van Dorp’s experiment, obtained a compound melting at 137°. Schultz, without regard to any existing discrepancies, gives the melting point as 55°. In order to settle the question, the author has reinvestigated the different processes by which orthoazotoluene may be formed. By the action of sodium amalgam on nitrotoluene, the product of direct nitric acid on toluene (which according to many investigators is a mixture of symmetrical [2:3] and ortho-nitrotoluene [1:3]), a mixture of two azotoluenes was obtained, of which one melts at 137° and the other at 55°. The latter crystallises in short, red prisms, which were scattered about amongst the long, orange needles of the former. Petrieff’s and Schultz’s method consists in the reduction of orthonitrotoluene with zinc-dust. Orthonitrotoluene was purified by repeated distillation, in order to get rid of the symmetrical modification, and the product boiling at 122—123°, the purity of which was confirmed by oxidation and by reduction, was dissolved in alcohol and treated with zinc-dust in the presence of aqueous soda. After adding water, an oil was obtained, which the following day became converted into thick, red needles, melting at 55°. According to Tutkoffsky, the crystals are rhombic; axial ratio $a:b:c = 0.875588:1:1.013960$; observed faces ∞P and $\bar{P}\infty$. They are ruby-red and pleochroic. By reduction with sodium-amalgam in alcoholic solution, this yielded colourless crystals of the hydrazo-compound (m. p. 161°), which on oxidation again gave the red

needles of orthoazotoluene (m. p. 55°). From this and other reactions, it follows that Petrieff's so-called "azoxytoluene" is this orthoazotoluene. Using Hoogewerff and van Dorp's method, the author subjected orthotoluidine to the action of potassium permanganate in alkaline solution, and the same azotoluene, melting at 55° , was obtained. Perkin's method, namely, distillation of nitrotoluene in alcoholic solution with sodium hydroxide, gives the same azotoluene (m. p. 55°), but the method cannot be recommended. From the results of these experiments it follows that orthoazotoluene melts at 55° ; 100 parts of alcohol at 14.5° dissolve 6.027 parts; 100 parts of ether at 16.5° dissolve 147.66 parts. It dissolves in sulphuric acid, and is separated again on addition of water; the same with the acetic acid solution. It absorbs benzene vapour, and deliquesces to a red liquid.

B. B.

Diazo-compounds. By P. GRIESS (*Ber.*, 21, 1559—1566).—

Paramidotriazobenzene, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}<\text{N}>$, is prepared from paraphenyleneamido-oxamic acid (*Abstr.*, 1885, 1220) in a manner exactly similar to the meta-derivative (*ibid.*, 788); it crystallises in long plates, readily soluble in the usual solvents, except water. It melts at 65° , and detonates at a higher temperature. When exposed to air it becomes reddish; it is completely decomposed by prolonged boiling with water. The *hydrochloride* crystallises in needles or plates, generally reddish; very readily soluble in cold water. The *platinochloride* forms bright yellow needles, very sparingly soluble in cold water.

Paradiazotriazobenzene was obtained by diazotising the amido-compound above described, but was not isolated. The *platinochloride*, $(\text{N}_2\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{N}_3)_2\cdot\text{PtCl}_4$, crystallises in long, narrow plates, which explode violently when heated. The *perbromide*, $\text{N}_3\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{Br}_3$, is formed when a mixture of bromic and hydrobromic acid is added to an aqueous solution of the hydrobromide; it separates as a red oil, which gradually crystallises.

Paraditriazobenzene (*parahezazobenzene*), $\text{C}_6\text{H}_4(\text{N}<\text{N}>)_2$ [1 : 4], is formed when paradiazotriazobenzene perbromide is added to aqueous ammonia. The whole is distilled, and the solid distillate crystallised from ether. It crystallises in colourless, well-formed plates, which melt at 83° , and become brown when exposed to light; it is very readily soluble in ether and chloroform, sparingly soluble in alcohol, and almost insoluble in water. It has a sweet taste. When heated above its melting point, it explodes with extreme violence. It is indifferent to bases and acids in the cold, but is decomposed by prolonged boiling with strong hydrochloric acid. The compound was not analysed, but the formula assigned to it is supported by the mode of formation of the substance, as well as by analyses of the analogously constituted hexazobenzoic acid described below. Hexazobenzene can also be prepared from paratetrazobenzene.

Metamidotriazobenzoic acid, $\text{COOH}\cdot\text{C}_6\text{H}_3(\text{NH}_2)\text{N}_3$ [= 1 : 3 : 5], is prepared by boiling 1 : 3 : 5 diamidobenzoic acid dissolved in hydrochloric acid with twice the amount of oxalic acid. The *amido-*

oxalamidobenzoic acid, $\text{COOH}\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{NH}\cdot\text{C}_2\text{O}_2\cdot\text{OH}$ (which forms white grains, almost insoluble in water), thus obtained is diazotised and the diazo-compound converted into the perbromide and treated with ammonia. On adding hydrochloric acid to the product, *metatriazo-oxalamidobenzoic acid*, $\text{COOH}\cdot\text{C}_6\text{H}_3(\text{N}_3)\cdot\text{NH}\cdot\text{C}_2\text{O}_2\cdot\text{OH}$, is liberated. This is a yellowish substance, rather readily soluble in hot water; when boiled with dilute aqueous potash, it is decomposed into *metamidotriazobenzoic* and *oxalic acids*. *Metamidotriazobenzoic acid* crystallises from water in slightly reddish needles, readily soluble in cold alcohol and ether, almost insoluble in cold water. It has a slightly acid taste, and detonates when heated in the dry state. The *hydrochloride* crystallises in small needles, very readily soluble in cold water; the *platinochloride* is also described.

Metadiazotriazobenzoic acid seems not to exist in the free state. The *nitrate*, $\text{COOH}\cdot\text{C}_6\text{H}_3(\text{N}_3)\cdot\text{N}_2\cdot\text{NO}_2$ [1 : 3 : 5], crystallises in well-formed, sparingly soluble prisms; the *perbromide*, $\text{C}_7\text{H}_4\text{N}_6\text{Br}_3$, and *platinochloride*, are also described.

Metadiazotriazoamidobenzene, $\text{COOH}\cdot\text{C}_6\text{H}_3(\text{N}_3)_2\cdot\text{N}_2\cdot\text{NHPh}$, is formed when *metadiazotriazobenzoic acid nitrate* is treated with aniline. It is very readily soluble in ether, insoluble in water, and has an intense yellow colour.

Metaditriazobenzoic acid (hexabenzoic acid), $\text{COOH}\cdot\text{C}_6\text{H}_3(\text{N}_3)_2$ [1 : 3 : 5], is prepared by dissolving *metadiazotriazobenzoic acid perbromide* in aqueous ammonia, and is purified by crystallisation from hot dilute alcohol (using animal charcoal), from which it separates in small, white needles, almost insoluble in boiling water, very readily soluble in ether. It has a bitter taste. When heated it explodes, with formation of a black cloud. It yields very stable salts. The *barium salt* forms almost insoluble, white needles.

Benzeneazodiphenyldisulphonic acid, $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, is obtained by dissolving *benzeneazodiphenyl* (1 part) (compare *Ber.*, 21, 911) in fuming sulphuric acid (3 to 4 parts), and heating the whole on a water-bath, until a sample is quite soluble in water. It is poured into water (6 parts), the yellowish-red crystals washed with hydrochloric acid and dried. The pure acid is prepared from the barium salt. It is readily soluble in alcohol and in cold water, and is precipitated from the latter by addition of hydrochloric acid. The *potassium salt* (with $1\frac{1}{2}$ mol. H_2O) crystallises in well-formed prisms, readily soluble in hot water; the *barium salt* forms a granulo-crystalline precipitate. The disulphonic acid is reduced by tin and hydrochloric acid, and by ammonium sulphide, with formation of a very sparingly soluble amido-acid, crystallising in narrow plates of a silvery lustre.

N. H. M.

Mixed Azo-compounds. By C. BEYER and L. CLAISEN (*Ber.*, 21, 1697—1705).—*Phenylazoacetoacetaldehyde*, $\text{COMe}\cdot\text{CH}(\text{CHO})\cdot\text{N}_2\text{Ph}$, is obtained by gradually adding a dilute solution of *diazobenzene chloride* to an aqueous solution of *sodacetoacetaldehyde*. It crystallises from boiling alcohol in thick, dark-red, or thin, lighter coloured prisms, according to the concentration of the solution. It melts at 118° , and gives a crystalline copper compound with copper

acetate. The *hydrazone*, $\text{COMe}\cdot\text{CH}(\text{N}_2\text{Ph})\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$, prepared by mixing an alcoholic solution with phenylhydrazine, is very sparingly soluble in alcohol, from which it crystallises in yellowish-red needles melting at 218° . When boiled with glacial acetic acid, it yields a compound, $\text{N}_2\text{Ph}\cdot\text{C}\leq\text{CH}\cdot\text{N}-\text{CMe}\cdot\text{NPh}>$, which crystallises from methyl alcohol in needles melting at 112° , and insoluble in alkalis.

An alkaline solution of phenylazoacetoacetaldehyde gives with an alkaline solution of phenylhydrazineparasulphonic acid a yellow, crystalline precipitate, probably sodium *phenylazoacetoacetaldehydehydrazideparasulphonate*, which in a sulphuric acid bath, shows the same shade as, although in a considerably less degree than, tartrazin.

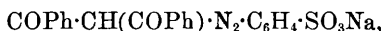
Phenylazoacetylacetone, $\text{COMe}\cdot\text{CH}(\text{COMe})\cdot\text{N}_2\text{Ph}$, prepared by mixing aqueous solutions of sodium acetylacetone and diazobenzene chloride, crystallises from boiling alcohol in long, yellow needles melting at 90° .

Phenylazophenyldimethylpyrazole, $\text{N}_2\text{Ph}\cdot\text{C}\leq\text{CMe}\cdot\text{N}-\text{CMe}\cdot\text{NPh}>$, is obtained by heating the preceding compound with phenylhydrazine at $130-140^\circ$. It crystallises from slightly acid alcohol in yellow needles, which melt at 63° and are insoluble in alkalis.

Phenylazodibenzoylmethane, $\text{COPh}\cdot\text{CH}(\text{COPh})\cdot\text{N}_2\text{Ph}$, is prepared by precipitating an aqueous alcoholic solution of sodium dibenzoylmethane with a dilute solution of diazobenzene chloride. It crystallises from boiling alcohol in yellowish-red prisms melting at $153-154^\circ$.

Phenylazotriphenylpyrazole, $\text{N}_2\text{Ph}\cdot\text{C}\leq\text{CPh}\cdot\text{N}-\text{CPh}\cdot\text{NPh}>$, obtained by heating the preceding compound with phenylhydrazine, crystallises from boiling alcohol in yellowish-red prisms, melts at $156-157^\circ$, and is insoluble in alkalis. It is more readily soluble in light petroleum and ethyl acetate than phenylazodibenzoylmethane.

Sodium phenylazodibenzoylmethaneparasulphonate,



is formed by the action of diazobenzenesulphonic acid on an alkaline solution of dibenzoylmethane. It crystallises from hot water in golden-yellow leaves, and when treated with mineral acids yields the free sulphonic acid in the form of a yellow, pasty mass of microscopic needles, which colour wool greenish in a sulphuric acid bath.

The above compounds are true phenylazo-derivatives, no intramolecular change, by which they would be converted into hydrazine-derivatives, having taken place. The phenylazo-derivatives are all soluble in alkali, but are precipitated from the solution by carbonic anhydride.

The following compounds are chemically and physically similar to those already described, and are also, probably, true phenylazo-derivatives.

Phenylazobenzoylaldehyde, $\text{COPh}\cdot\text{CH}(\text{CHO})\cdot\text{N}_2\text{Ph}$, crystallises from alcohol in yellow or dark-red prisms melting at 103° .

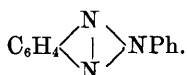
Phenylazobenzoylacetone, $\text{COPh}\cdot\text{CH}(\text{COMe})\cdot\text{N}_2\text{Ph}$, crystallises from alcohol in yellowish-red prisms melting at 99° .

Ethyl phenylazoacetylpyruvate, $\text{COMe}\cdot\text{CH}(\text{CO}\cdot\text{COOEt})\cdot\text{N}_2\text{Ph}$, crystallises from alcohol in yellow prisms melting at $115-116^\circ$.

Ethyl phenylazobenzoylpyruvate, $\text{COPh}\cdot\text{CH}(\text{CO}\cdot\text{COOEt})\cdot\text{N}_2\text{Ph}$, crystallises from alcohol in yellowish-red prisms melting at $116-117^\circ$.

F. S. K.

Two Bye-products in the Technical Preparation of Amidoazobenzene. By L. GATTERMANN and G. WICHMANN (*Ber.*, 21, 1633—1637).—The aniline recovered from the acid solution obtained in the preparation of amidoazobenzene contains amidodiphenyl sulphate and a new compound of the formula $\text{C}_{12}\text{H}_9\text{N}_3$. The latter is obtained by extracting the crude product with glacial acetic acid; on adding water to the acetic acid solution, the compound separates in lustrous needles. Its molecular weight was determined by Raoult's method. It dissolves readily in the usual solvents, melts at 109° , and boils without decomposition. It is not dissolved by acids or alkalis, and does not react with acid chlorides and with nitrous acid; it can be distilled over zinc-dust without change. When reduced with sodium in alcoholic solution, aniline and orthophenylenediamine are formed. The compound is therefore an azimide of the formula



The *nitro-derivative*, $\text{C}_{12}\text{H}_8\text{N}_4\text{O}_2$, prepared by slightly warming 2 grams of the substance with 10 c.c. of strong sulphuric acid, crystallises from glacial acetic acid in white needles melting at 275° .

The presence of amidodiphenyl sulphate is accounted for by the fact that the crude hydrochloric acid in which the aniline is dissolved, contains sulphuric acid.

N. H. M.

Phenylhydrazines. By C. WILLGERODT and M. FERKO (*J. pr. Chem.* [2], 37, 345—358).—*Picrylhydrazine* is best prepared by carefully mixing picryl chloride (1 mol.) and phenylhydrazine (2 mols.) in cold alcoholic solution. It forms pale-red scales melting at 172° . If the solution is warmed, decomposition takes place, and the melting point of the product is considerably raised. On boiling picrylhydrazine with acetic acid, strong hydrochloric acid, or dilute sulphuric acid for a short time, *dinitrosonitroazobenzene*, $\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{NO})_2\cdot\text{NO}_2$, crystallising in golden-yellow scales melting at 247.5° is formed, together with a substance of a brownish colour, melting at 145° , not yet investigated. On boiling with alcohol, picrylphenylhydrazine yields what is probably a mixture of trinitrohydrazobenzene, nitroso-dinitrohydrazobenzene, and nitrosodinitroazobenzene.

Dinitrosonitroazobenzenesulphonic acid is formed by heating a mixture of dinitrosonitroazobenzene (5 grams) with equal parts (15 grams) of ordinary and fuming sulphuric acid at $220-230^\circ$. The acid crystallises from water in yellow needles, and from acetic acid in yellow scales, which do not melt at 360° .

α -Dinitrohydrazobenzene, $\text{N}_2\text{H}_2\text{Ph}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$, is best prepared by digesting finely-powdered α -dinitrochlorobenzene (5 grams) with phenylhydrazine (5.5 grams) in alcoholic solution for eight days. It

crystallises from hot alcohol in beautiful red scales melting at 120°. When shaken with mercuric oxide, it yields α -dinitroazobenzene, which crystallises from alcohol in small needles melting at 116—117° (uncorr.).

Dinitrosoazobenzene may be prepared by heating α -dinitrochlorobenzene with phenylhydrazine and alcohol in sealed tubes at 120—130°. It crystallises in needles of a brownish colour melting at 175°.

Orthonitrometachlorhydrazobenzene is formed when Laubenheimer's dinitrochlorobenzene (3 grams) is heated with phenylhydrazine (3.3 grams) and alcohol. It crystallises in short, red prisms melting at 139—140° (uncorr.).

Orthonitrometachlorazobenzene, $\text{Ph} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{NO}_2\text{Cl}$ [$\text{N} : \text{NO}_2 : \text{Cl} = 1 : 2 : 5$], is prepared by treating the preceding hydrazo-compound with mercuric oxide. It forms small, red needles melting at 94°.

Orthonitrosometachlorazobenzene is formed by boiling the corresponding hydrazo-compound with water or acids. It melts at 136—137°.

The authors have failed in their attempts to obtain an unsymmetrical picrylhydrazine by heating together picryl chloride (8.6 grams) and phenylhydrazine (5 grams) in alcoholic solution. G. T. M.

New Method for the Preparation of Biguanides. Derivatives of Phenylbiguanide. By A. SMOLKA and A. FRIEDREICH (*Monatsh.*, 9, 227—241).—The hydrochlorides of biguanide, ethylbiguanide, and phenylbiguanide can be prepared by heating an alcoholic solution of dicyandiamide with ammonium chloride, ethylamine hydrochloride, and aniline hydrochloride respectively.

Copper phenylbiguanide, $(\text{C}_6\text{H}_{10}\text{N}_5)_2\text{Cu} + 1\frac{1}{2}\text{H}_2\text{O}$, is obtained by treating the hydrochloride (see below) with warm soda. It is a dark-rose coloured, microscopic, crystalline powder, which decomposes and turns brown when boiled with water, or, more quickly, when heated alone at 130—135°. It is very sparingly soluble in cold, more readily soluble in hot water; the aqueous solution absorbs carbonic anhydride from the air and becomes turbid owing to the separation of the carbonate. It has strongly basic properties, liberates ammonia from its salts, precipitates metallic hydroxides from solutions of metallic salts, and combines with acids. The *hydrochloride*, $(\text{C}_6\text{H}_{10}\text{N}_5)_2\text{Cu} \cdot 2\text{HCl} + 1\frac{1}{2}\text{H}_2\text{O}$, prepared by digesting phenylbiguanide hydrochloride with freshly-precipitated copper hydroxide, crystallises in carmine-red aggregates which slowly decompose when heated above 140°. It is readily soluble in water, but is decomposed with separation of a brown product, when the solution is boiled for some time. Alkalis give rose-coloured precipitates of the copper base when added to the aqueous solution and soluble sulphates, carbonates, phosphates, chromates, and oxalates precipitate the corresponding salt of copper phenylbiguanide. The *sulphate*, $(\text{C}_6\text{H}_{10}\text{N}_5)_2\text{Cu} \cdot \text{H}_2\text{SO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, forms rose-coloured, microscopic needles which decompose when heated at about 150°. It is not decomposed when boiled with water, in which it is very sparingly soluble. The *chromate*, $(\text{C}_6\text{H}_{10}\text{N}_5)_2\text{Cu} \cdot \text{H}_2\text{CrO}_4 \cdot \text{H}_2\text{O}$, is a yellowish-green, microscopic, granular powder, which decomposes when heated at about 150°. It is more sparingly soluble in water than the sulphate, and does not decompose when boiled with water.

Nickel phenylbiguanide, $(C_8H_{10}N_5)_2Ni$, prepared by precipitating the hydrochloride with soda, is a yellow powder which is almost totally insoluble in water, and is not decomposed either when heated at 150° or when boiled with water. The *hydrochloride*, $(C_8H_{10}N_5)_2Ni \cdot 2HCl$, prepared in like manner to the copper salt, forms yellow, granular crystals which are readily soluble in water and decompose when heated to about 150° . The aqueous solution is yellow, decomposes when heated, and behaves towards reagents similarly to the corresponding copper salt. The *sulphate*, $(C_8H_{10}N_5)_2Ni \cdot H_2SO_4 + 1\frac{1}{2}H_2O$, crystallises in orange-yellow, microscopic plates which decompose when heated at about 150° . It is very sparingly soluble in water, and is not decomposed when boiled with it.

Cobalt phenylbiguanide, $(C_8H_{10}N_5)_2Co + 1\frac{1}{2}H_2O$, is a dark-rose coloured, microscopic, granular powder, which is far more readily soluble in water than the copper or nickel base. It forms large, raspberry-red leaves when a dilute aqueous solution is evaporated slowly; it has strongly basic properties. It is decomposed when heated at about 145° or when boiled with water. The *hydrochloride*, $(C_8H_{10}N_5)_2Co \cdot 2HCl + 1\frac{1}{2}H_2O$, forms small, raspberry-red plates which are tolerably easily soluble in water, forming a wine-red coloured solution. It is decomposed when boiled with water or when heated at about 150° , and it behaves towards reagents like the corresponding copper and nickel salts. The *sulphate*, $(C_8H_{10}N_5)_2Co \cdot H_2SO_4 + H_2O$, forms silky, carmine-red needles which are sparingly soluble in water, and decompose when heated to about 150° . It is not decomposed when boiled with water. F. S. K.

Safranines and related Dyes. By R. NIETZKI and R. OTTO (*Ber.*, 21, 1590—1598; compare *Abstr.*, 1887, 250).—When an alcoholic solution of phenosafranine is treated with sulphuric acid just sufficient to produce a violet coloration, and boiled with an excess of sodium nitrite, a magenta-coloured solution is obtained which is not fluorescent. The new compound thus obtained is less strongly basic than safranine, and can be liberated from its salts by caustic alkalis, but not by carbonates. It is purified by precipitation with zinc chloride and hydrochloric acid. The *nitrate*, $C_{18}H_{13}N_3 \cdot HNO_3$, *sulphate*, $C_{18}H_{13}N_3 \cdot H_2SO_4$, and *platinochloride* were prepared. The *acetyl-derivative* is violet, and yields yellow, sparingly soluble salts. The compound $C_{18}H_{13}N_3$, in the form of its salts, dissolves in water with red colour, and dyes wool and silk red, but with a much more bluish shade than safranine does. Hydrochloric acid dissolves it with green coloration which changes at once to red on addition of water.

The *phenosafranine base*, $C_{18}H_{16}N_4O$, is prepared by treating the sulphate with the exact amount of baryta. On evaporating the solution with exclusion of air, plates of a golden lustre separate: it is best to evaporate in a vacuum at 40° . It is readily soluble in alcohol, sparingly soluble in water, and almost insoluble in ether. Water decomposes it with formation of the base $C_{18}H_{14}N_4$.

Safranol, $C_{18}H_{19}N_2(OH)_2$, is obtained by boiling phenosafranine hydrochloride with an excess of alcoholic potash for three days; the alcohol is evaporated, water and then an excess of acetic acid

added; the brown crystals thus obtained are dissolved in ammonia and precipitated with hydrochloric acid. It separates in large, brass-coloured needles, is almost insoluble in water, alcohol, and glacial acetic acid, but readily soluble in caustic alkali and ammonia, with carmine-red colour. Strong sulphuric acid dissolves it with brown colour. The *diacetyl*-derivative crystallises in plates of a metallic lustre, insoluble in ammonia. When phenosafranine is boiled for several days with zinc-dust and hydrochloric acid, the compound $C_{18}H_{19}N_3O$ is formed. This crystallises from water in long, colourless needles, readily soluble in alcohol, less soluble in ether, benzene, and hot water, and melts at 130° , losing water. No crystalline salts could be obtained. The *acetyl*-derivative, $C_{18}H_{18}N_3OAc$, forms broad needles melting at 173° , readily soluble in acids, and yields a yellow crystalline *platinochloride*, $(C_{18}H_{18}N_3OAc)_2 \cdot H_2PtCl_6$. When a solution of the base in an excess of dilute sulphuric acid is treated with sodium nitrite and then with alcohol, a new *base*, of the formula $C_{18}H_{18}N_2O$, is obtained. The latter crystallises from dilute alcohol in broad needles melting at 117° ; it yields no *acetyl*-derivative, and cannot be diazotised. The *platinochloride*, $(C_{18}H_{18}N_2O)_2 \cdot H_2PtCl_6$, is sparingly soluble.

The behaviour of the base, $C_{18}H_{19}N_3O$, when heated makes it probable that the oxygen in it is present in the form of water, and that the compound, as well as the compound $C_{18}H_{18}N_2O$, are the respective hydrates of the bases $C_{18}H_{17}N_3$ and $C_{18}H_{16}N_2$. N. H. M.

Chemical Process which takes place in the Dyeing of Wool and Silk with Basic Coal-tar Dyes. By E. KNECHT (*Ber.*, **21**, 1556—1558).—In order to determine whether the taking up of dyes by fibres is a mechanical or chemical process, quantitative experiments were made in which wool and silk respectively were boiled with solutions of weighed amounts of rosaniline hydrochloride, diamido-azobenzene hydrochloride, and methyl violet. 0.2 gram of rosaniline hydrochloride was dissolved in 500 c.c. of water and boiled with wool until the solution was colourless. The liquid was then neutral and contained ammonia. A hydrochloric acid determination showed that the whole of the hydrochloric acid originally in the magenta remained in the decolorised solution. Similar results were obtained from the other experiments. The taking up of dyes by animal fibres involves, therefore, a quantitative chemical change, and is not a mechanical process merely. It is probable that very complex compounds are formed. N. H. M.

Derivatives of Diphenylphosphorous Chloride and Diphenylphosphine. By C. DÖRKEN (*Ber.*, **21**, 1505—1515).—*Diphenylbenzylphosphine chloride*, $C_7H_7 \cdot PPh_2Cl_2$, obtained by heating diphenylphosphorous chloride at 180° with excess of benzyl chloride, forms slightly yellow prisms, melts at 187° , and is insoluble in ether and benzene. When treated with alcohol or water, it is quickly converted into diphenylbenzylphosphine oxide, melting at 195 — 196° .

Diphenyldimethylphosphonium iodide, $\text{PMe}_2\text{Ph}_2\text{I}$, is prepared by heating diphenylphosphorous chloride with methyl iodide.

Trinitrodiphenylbenzylphosphine oxide, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{P}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, formed by treating the oxide with a mixture of fuming nitric acid and concentrated sulphuric acid, separates from glacial acetic acid in colourless crystals which melt at 206° , are insoluble in alcohol, ether, &c., but moderately soluble in glacial acetic acid. Diphenylphosphine can be obtained by heating diphenylphosphorous chloride at 230° with zinc. It is a colourless, oily liquid of disagreeable odour, insoluble in water, but readily soluble in ether, alcohol, and benzene. On exposure to the air, it is oxidised to diphenylphosphinic acid. It combines with methyl iodide, acetic chloride, and benzoic chloride.

Diphenylphosphonium chloride, $\text{PH}_2\text{Ph}_2\text{Cl}$, obtained in the form of a white, crystalline mass by treating diphenylphosphorous chloride with hydrogen chloride, is sparingly soluble in ether and quickly decomposes on exposure to the air. The *platinochloride*, $(\text{PH}_2\text{Ph}_2\text{Cl})_2\cdot\text{PtCl}_4$, is a yellow powder.

Diphenylphosphonium iodide, formed by the combination of diphenylphosphine with concentrated hydriodic acid, is a yellowish-white, unstable compound.

Tetraphenyldiphosphine, $\text{PPh}_2\cdot\text{PPh}_2$, obtained by warming diphenylphosphorous chloride with diphenylphosphine, melts at 67° , boils at about 400° , and gradually oxidises on exposure to the air. It is converted into diphenylphosphinic acid when warmed with nitric acid. Diphenylphosphine and carbon bisulphide combine when heated together, to form a compound $\text{PPh}_2\cdot\text{CS}\cdot\text{S}\cdot\text{PPh}_2$, which crystallises from warm alcohol in shining forms melting at 157° . It is readily soluble in carbon bisulphide, glacial acetic acid, and warm alcohol, but insoluble in ether.

Paradiphenyltolylphosphine, $\text{PPh}_2\cdot\text{C}_6\text{H}_4\text{Me}$, prepared by the action of sodium on a mixture of diphenylphosphorous chloride and parabromotoluene in ethereal solution, crystallises from ether or alcohol in colourless prisms melting at 68° . It is a feeble base, dissolves readily in concentrated hydrochloric acid, but is reprecipitated from the solution by water.

Diphenyltolylphosphine oxide, $\text{POPh}_2\cdot\text{C}_6\text{H}_4\text{Me}$, is obtained by treating the phosphine first with bromine and then with alkali. It crystallises from alcohol, melts at $129\text{--}130^\circ$, and is only sparingly soluble in ether.

Diphenyltolylphosphine sulphide, $\text{PSPPh}_2\cdot\text{C}_6\text{H}_4\text{Me}$, is formed when a carbon bisulphide solution of the phosphine and sulphur is evaporated. It crystallises from alcohol in long, silky needles, which melt at 139° , are readily soluble in carbon bisulphide, moderately soluble in alcohol, but insoluble in ether.

Di-tolylphenylphosphine, $\text{PPh}(\text{C}_6\text{H}_4\text{Me})_2$, obtained by the action of sodium on an ethereal solution of phenyl chloride and parabromotoluene, crystallises from alcoholic ether in small, colourless needles, melts at 57° , and is readily soluble in ether, but only sparingly in alcohol.

Dinitrodiphenylphosphinic acid, $(\text{NO}_2\cdot\text{C}_6\text{H}_4)_2\text{PO}\cdot\text{OH}$, is prepared by treating diphenylphosphinic acid with a mixture of concentrated

sulphuric acid and fuming nitric acid. It melts at 268° , and is only sparingly soluble in alcohol, ether, benzene, and glacial acetic acid. When heated in a test-tube, it explodes. The *ammonium* salt, $(\text{C}_6\text{H}_4\text{NO}_2)_2\text{PO}\cdot\text{ONH}_4$, crystallises in small, yellow columns which melt at 260° , and are sparingly soluble in alcohol and cold water. The *potassium* salt, $(\text{C}_6\text{H}_4\text{NO}_2)_2\text{PO}\cdot\text{OK} + 2\text{H}_2\text{O}$, is a yellow, crystalline powder, which is readily soluble in water, but more sparingly soluble in alcohol. The *barium*, *lead*, and *silver* salts are yellowish, crystalline compounds.

Diamidodiphenylphosphinic acid, obtained by reducing the nitro-compounds, forms small, brown crystals, melts at 276° with decomposition, and is only sparingly soluble in almost all solvents.

F. S. K.

Derivatives of Dimethylaniline containing Phosphorus; and Mercury Dimethylaniline. By A. SCHEUK and A. MICHAELIS (*Ber.*, **21**, 1497—1504).—*Dimethylamidophenylphosphorous chloride*, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{PCl}_2$ [$\text{PCl}_2 : \text{NMe}_2 = 1 : 4$], is obtained by mixing phosphorus trichloride with dimethylaniline and gradually adding aluminium chloride. It forms a slightly yellow, deliquescent, crystalline mass, melts at 66° , and boils at 250° (120 mm. pressure) with partial decomposition. It is sparingly soluble in light petroleum, more readily soluble in ether, and readily soluble in benzene and phosphorus trichloride. It dissolves in water with evolution of heat and a strong phosphine smell. A white powder, probably the *hydrochloride*, $\text{PCl}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\text{HCl}$, soon separates from solutions of this compound owing to absorption of moisture.

Sodium dimethylamidophenylphosphinite, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{PO}_2\text{HNa} + 2\text{H}_2\text{O}$, obtained by evaporating an aqueous solution of the preceding compound and treating the residue with soda, forms large well-defined crystals.

Dimethylamidophenylphosphinous acid, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{PO}_2\text{H}_2$, prepared by decomposing the lead salt with hydrogen sulphide, crystallises in white needles which melt at 162° , are readily soluble in water and hot alcohol, but only sparingly in cold alcohol. The acid is decomposed into dimethylaniline and phosphorous acid when heated in aqueous or dilute hydrochloric acid solution, but it is very stable in alkaline or alcoholic solution. Dimethylaniline, phosphorus and hydrogen phosphide are obtained when the acid is heated alone.

Dimethylamidophenylphosphonic acid, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{PO}(\text{OH})_2$, is prepared by oxidising sodium dimethylamidophenylphosphinite in alcoholic solution with mercuric chloride. From alcohol, it separates in crystals which melt at 133° , and are readily soluble in water and alcohol. In aqueous solution this acid seems to be as unstable as dimethylamidophenylphosphinous acid.

Paramercurodimethylaniline, $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, is formed when parabromodimethylaniline is dissolved in coal-tar xylene, ethyl acetate added, and the mixture boiled with sodium amalgam. It crystallises from benzene and alcoholic benzene with 1 mol. of benzene in slightly yellow needles which quickly become dull and crumble to a white powder on exposure to the air, owing to the volatilisation of the benzene. It melts at 169° , is sparingly soluble in alcohol and ether,

but dissolves readily in benzene and chloroform. Soda precipitates the base unchanged from its solution in dilute hydrochloric acid, but when heated with hydrochloric acid it is decomposed. When treated with phosphorus trichloride, it yields dimethylamidophenylphosphorous chloride.

Dimethylamidotriphenylphosphine, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{PPh}_2$, is formed by the action of sodium on a benzene solution of dimethylamidophenylphosphorous chloride and chlorobenzene. It crystallises from hot alcoholic ether in forms which melt at 152° , are readily soluble in benzene, but tolerably sparingly soluble in alcohol and ether. This compound is only a feeble base, and is precipitated from its solution in concentrated hydrochloric acid by water. It combines readily with benzyl chloride and alkyl iodides, and can be readily converted into the corresponding oxide and sulphide.

Hexamethyltriamidotriphenylphosphine, $\text{P}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_3$ (Hannemann, this Journal, 1877, ii, 417), is obtained as a bye-product in the preparation of dimethylamidophenylphosphorous chloride. It forms slender, colourless needles, melts at 273° , and turns blue on exposure to the air. It is a very stable compound, is sparingly soluble in cold, more readily in hot alcohol, and is readily soluble in chloroform and dilute hydrochloric acid.

A white powder, $\text{C}_{12}\text{H}_{10}\text{NPO}$, is formed when diphenylamine and phosphorus trichloride are heated with zinc chloride in sealed tubes. This compound yields nitro- and amido-derivatives which are, however, very sparingly soluble and mostly amorphous.

F. S. K.

Xylylphosphorus Compounds and Toluphosphonic Acids.

By J. WELLER (*Ber.*, 21, 1492—1497; compare *Abstr.*, 1887, 824).—*Lead α -toluphosphonate*, $\text{COOH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{PO} \cdot \text{O}_2 \cdot \text{Pb} + \text{H}_2\text{O}$, crystallises from dilute acetic acid in transparent needles which are insoluble in water. *Silver α -toluphosphonate* and *silver β -toluphosphonate*,



are white, amorphous compounds which are sparingly soluble in water, but readily soluble in ammonia and nitric acid.

β -Toluphosphonic acid chloride, $\text{COCl} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{POCl}_2$, formed by the action of phosphorus pentachloride on the acid, boils at 249° (147 mm. pressure), and is readily decomposed by water.

Paraxylylphosphorous chloride, $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{PCl}_2$, prepared by acting on a mixture of phosphorous chloride and paraxylene with aluminium chloride, is a colourless, strongly refractive liquid which boils at 253 — 254° , and solidifies at -30° to colourless needles.

Paraxylylphosphorous tetrachloride, $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{PCl}_4$, produced when the preceding compound is treated with chlorine, forms a colourless or slightly yellow mass which melts at 60° .

Paraxylylphosphorous oxychloride, $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{POCl}_2$, is formed by treating the tetrachloride with water or sulphurous anhydride. It is a thick, colourless liquid which boils at 280 — 281° .

Paraxylylphosphinous acid, $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{PO}_2\text{H}_2$, is formed when the corresponding chloride is treated with warm water.

Paraxylylphosphonic acid, $C_6H_3Me_2 \cdot PO(OH)_2$, obtained by decomposing paraxylyltetra- or oxy-chloride with water, crystallises in colourless needles and melts at $179-180^\circ$. It is moderately soluble in water, dissolves readily in alcohol, but is only sparingly soluble in ether. When heated, it is decomposed, yielding metaphosphoric acid and paraxylene. The acid potassium salt, $C_6H_3Me_2 \cdot PO_3HK$, and the barium salt, $C_6H_3Me_2 \cdot PO_3Ba$, are crystalline.

Paranitroxylphosphonic acid, $NO_2 \cdot C_6H_2Me_2 \cdot PO(OH)_2$, is prepared by nitrating the acid. It crystallises in needles, melts at 224° , and is readily soluble in alcohol, but only sparingly in ether.

Paratolulphosphonic acid, $COOH \cdot C_6H_3Me \cdot PO(OH)_2$, is formed when paraxylylphosphonic acid is oxidised with potassium permanganate in alkaline solution. It crystallises from dilute alcohol in colourless or slightly yellow, slender needles melting at 278° . It is readily soluble in alcohol, sparingly soluble in water, and almost insoluble in ether. When heated, it yields paratoluic acid and metaphosphoric acid with partial decomposition.

Paratolulphosphonic chloride, $COCl \cdot C_6H_3Me \cdot POCl_2$, forms a colourless crystalline mass which melts at 62° , and is readily decomposed by water.

F. S. K.

Action of Methylamine and Ethylamine on Salicaldehyde.

By M. DENNSTEDT and J. ZIMMERMANN (*Ber.*, **21**, 1553—1554).—When a slow stream of methylamine (1 mol.) is passed through salicaldehyde, yellow crystals of the additive compound (corresponding with aldehyde-ammonia) separate. Subsequently the liquid becomes warm, the crystals redissolve, and a separation of water takes place. The product of the reaction is extracted with ether and dried with calcium chloride; on distilling off the ether, a yellow oil is obtained of the composition represented by the formula C_8H_9NO . It boils at 229° . When treated with zinc chloride, it yields only a resin.

In a similar manner, ethylamine reacts with salicaldehyde with formation of the compound $C_9H_{11}NO$. This is a heavy, yellow oil which is soluble in water and boils at 237° .

N. H. M.

Tetrachlorobenzoic Acid from Tetrachlorophthalic Acid.

By P. TUST (*Ber.*, **21**, 1532—1534; compare *Abstr.*, 1887, 1046).—Barium tetrachlorobenzoate, $(C_6HCl_4 \cdot COO)_2Ba + 3\frac{1}{2}H_2O$, is moderately soluble in hot water, from which it crystallises in colourless, concentric needles which crumble on exposure to the air.

Tetrachloraniline, $C_6HCl_4 \cdot NH_2$ [$Cl_4 = 2 : 3 : 4 : 5$], is obtained when tetrachloranthranilic acid is heated. The last-named compound is prepared by nitrating tetrachlorobenzene and reducing the nitro-derivative obtained. The product is saturated with alkali and distilled with steam, when tetrachloraniline separates as a white, crystalline mass. It is easily soluble in alcohol, ether, benzene, and glacial acetic acid, but more sparingly in light petroleum, from which it crystallises in concentrically grouped needles melting at 118° .

Tetrachloracetanilide, $C_6HCl_4 \cdot NHAc$, crystallises from glacial acetic

acid in colourless, shining needles, melts at 154° , and is readily soluble in alcohol, ether, and glacial acetic acid. F. S. K.

Metahomo-anthranilic Acid and its Derivatives. By S. NIEMENTOWSKI (*Ber.*, **21**, 1534—1541). — *Orthonitroparatolunitrile*, $[\text{CN} : \text{NO}_2 : \text{Me} = 1 : 2 : 4]$, is obtained from the corresponding toluidine by Sandmeyer's method. It is very sparingly soluble in boiling water, from which it crystallises in long, yellow needles melting at 101° . It dissolves easily in all organic solvents, and can be sublimed or distilled with steam.

Orthamidoparatolunitrile, $[\text{CN} : \text{NH}_2 : \text{Me} = 1 : 2 : 4]$, prepared by reducing the nitro-compound with tin and hydrochloric acid, crystallises from dilute alcohol in thin, mostly hexagonal leaves, but sometimes in short, lance-shaped forms melting at 94° . It is insoluble in cold, but soluble in hot water, and readily soluble in alcohol, chloroform, acetone, benzene, ether, and light petroleum. It yields metatoluidine, ammonia, and carbonic anhydride when heated at 180° with hydrochloric acid. The *acetyl*-derivative, $\text{CN} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NHAc}$, which melts at 133° , is insoluble in cold, and only sparingly soluble in hot, water. It is easily soluble in alcohol, acetone, benzene, chloroform, ether, and light petroleum, but insoluble in cold acids and alkalis.

Orthamidoparatoluylamide, $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CONH}_2$ $[\text{CONH}_2 : \text{NH}_2 : \text{Me} = 1 : 2 : 4]$, is prepared by heating orthamidoparatolunitrile with dilute potash until the whole has just dissolved. It crystallises in white, very thin leaves or silky needles, melts at 146 — 147° , and is readily soluble in alcohol, acetone, chloroform, boiling water, and boiling benzene, sparingly soluble in boiling light petroleum, and insoluble in carbon bisulphide. The *hydrochloride* crystallises in needles which are very readily soluble in water.

Anhydracetylorthamidoparatoluylamide (β -methyl- δ -hydroxymetatolquinazoline), $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}$, is obtained when orthamidoparatoluylamide is boiled with an excess of acetic anhydride. It crystallises from boiling water in long, slender, white needles, melts at 255° , and is easily soluble in alcohol, acetone, chloroform, boiling benzene, and acids, but sparingly in ether, boiling water, and boiling light petroleum.

A similarly constituted condensation product is formed from orthamidoparatoluylamide and ethyl acetoacetate.

Tolylazimide, $\text{C}_6\text{H}_3\text{Me} \cdot \text{N} \begin{smallmatrix} \text{CO} \\ \text{N} \cdot \text{N} \end{smallmatrix} \text{NH}$, is formed by the action of nitrous acid on orthamidoparatoluylamide. It crystallises in long, white needles, melts at 226° with decomposition, and is almost totally insoluble in water, sparingly soluble in benzene, but dissolves easily in alcohol and boiling chloroform. It dissolves in very dilute alkalis and in concentrated acids, but is precipitated unchanged on adding water to its solution in acids.

Metahomo-anthranilic acid, $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{COOH}$ $[\text{COOH} : \text{NH}_2 : \text{Me} = 1 : 2 : 4]$, prepared by boiling orthamidoparatolunitrile or the corresponding amide with potash until the evolution of ammonia ceases, crystallises from alcohol in needles or leaves, which melt at 177° with evolution of carbonic anhydride. It is very easily soluble in

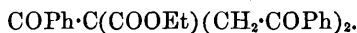
boiling alcohol, ether, and benzene, but only sparingly in boiling water, light petroleum, and carbon bisulphide. It forms salts both with acids and bases, and is converted into metabomosalicylic acid, melting at 174° , by the action of nitrous acid. When heated with carbamide, it yields a condensation product which melts at 360° ; when boiled with ethyl acetoacetate, a compound is obtained which crystallises from alcohol in long, slender needles. The *acetyl*-derivative crystallises from dilute alcohol in thick needles, melts at 183° , and is readily soluble in alcohol, chloroform, and boiling benzene, but only sparingly in water and light petroleum. *Ammonium orthacetamidoparatoluate* crystallises in needles which are very soluble in water. The *silver* salt is a white, crystalline compound which is sparingly soluble in boiling water. F. S. K.

Anhydrides of Cresotic Acid. By G. BARGIONI and H. SCHIFF (*Annalen*, 245, 42—44).—By the action of phosphorus oxychloride on α -cresotic acid, two anhydrides appear to be formed. The authors regard the portion soluble in alcohol as *tetracresotide*, $C_{37}H_{26}O_9$, and the insoluble portion as *hexacresotide*, $C_{48}H_{38}O_{13}$. The former melts at about 130° and the latter at about 250° . At 160° , ammonia converts hexacresotide into a mixture of ammonium creasotate and α -cresotamide, $OH \cdot C_6H_3Me \cdot CONH_2$ [$Me : OH : CONH_2 = 1 : 4 : 5$]. Aniline converts the hexacresotide into α -cresotanilide. This substance melts at 53° and forms crystalline scales. W. C. W.

Dicresoldicarboxylic Acid. By A. DENINGER (*Ber.*, 21, 1639—1641).—*Dicresoldicarboxylic acid*, $C_{16}H_{14}O_8$, is prepared by neutralising orthodicresol with alcoholic soda, drying the product at 180° in a stream of hydrogen, and heating it in an autoclave with carbonic anhydride for four hours at 160° , when the reaction takes place almost quantitatively. The product is dissolved in water and precipitated with hydrochloric acid; it is twice crystallised from pyridine, the salt then decomposed with hydrochloric acid, and the free acid crystallised from alcohol. It is insoluble in water, sparingly soluble in alcohol, ether, and chloroform, and does not melt at 290° . It gives a blue reaction with ferric chloride. The salts of the alkalis are readily soluble and amorphous; the salts of the heavy metals are insoluble in water, and are also amorphous. The *diacetyl*-compound, $C_{20}H_{18}O_8$, crystallises in needles decomposing at 163° , insoluble in water, sparingly soluble in alcohol.

Dinitroresol, $C_{14}H_{12}N_2O_6$ (Gerber, this vol., p. 484), is obtained by heating finely powdered dicresoldicarboxylic acid with nitric acid (sp. gr. = 1.3) until gas is evolved. It crystallises from pyridine in well-formed, reddish-yellow needles which may be washed with alcohol or ether, but which, when kept in a desiccator, gives up pyridine without losing their form; the decomposition is also brought about by water or, better, by aqueous hydrochloric acid. The free nitrophenol is soluble in toluene and in glacial acetic acid. It is very readily reduced by zinc and acetic acid to the corresponding diamide. N. H. M.

Ethyl Phenacylbenzoylacetate. By S. KAPF and C. PAAL (*Ber.*, 21, 1485—1492; compare *Abstr.*, 1884, 598, 1117; and 1885, 248).—*Ethyl phenacylbenzoylacetate*, $\text{COPh}\cdot\text{CH}(\text{COOEt})\cdot\text{CH}_2\cdot\text{COPh}$, is obtained by the action of phenacyl bromide (acetophenone bromide) on ethyl sodiobenzoylacetate. It is insoluble in water, but soluble in almost all ordinary organic solvents, and crystallises from ether or light petroleum in large, transparent, well-defined forms melting at $55\text{--}56^\circ$. When treated with dilute potash at the ordinary temperature, it yields benzoic acid and benzoylpropionic acid; if a slightly impure product is hydrolysed, an insoluble residue is formed, from which a crystalline product melting at $142\text{--}145^\circ$ is obtained. This compound appears to be *ethyl diphenacylbenzoylacetate*,



Phenylacetylenebenzoylactic acid, $\text{COPh}\cdot\text{CH}(\text{COOH})\text{C}:\text{CPh}$, is formed when the preceding compound is treated with alcoholic potash, or when it is distilled in a vacuum. This acid is insoluble in water, sparingly soluble in light petroleum, but dissolves tolerably readily in hot alcohol, ether, benzene, and glacial acetic acid. It crystallises in yellow needles, melts at 135° , and can be distilled in small quantities with slight decomposition. The *potassium salt*, $\text{C}_{17}\text{H}_{11}\text{O}_3\text{K} + 2\text{H}_2\text{O}$, is very sparingly soluble in cold, more readily in hot, water, and crystallises in very thin, yellow, long, flexible needles or threads. It is tolerably readily soluble in hot alcohol, but insoluble in an excess of alkali. An aqueous solution of the salt gives precipitates with the chlorides of calcium, barium, and mercury, with the sulphates of manganese and copper, and with silver nitrate.

$\alpha\text{-}\alpha'$ -*Diphenylfurfuran- β -carboxylic acid*, $\text{O} < \overset{\text{CPh}}{\text{CPh}} \text{CH} > \text{C}\cdot\text{COOH}$, is produced when phenylacetylenebenzoylactic acid is boiled with fuming hydrochloric acid and a little alcohol. It crystallises from alcohol in white needles, melts at 217° , and can be distilled with only slight decomposition. This acid is insoluble in water and light petroleum, but dissolves tolerably readily in warm ether, alcohol, glacial acetic acid, or benzene. It yields benzoic acid when oxidised with potassium permanganate in alkaline solution. The *sodium salt*, $\text{C}_{17}\text{H}_{11}\text{O}_3\text{Na}$, is readily soluble in alcohol or warm water, but is precipitated from its aqueous solution in slender needles by an excess of alkali. An aqueous solution gives precipitates with the chlorides of calcium, zinc, mercury, manganese, barium, and iron; with the sulphates of magnesium, iron, and copper, and with silver nitrate. The *ethyl salt* crystallises from ether in large forms melting at 82° .

2 : 5 *Diphenylfurfuran*, $\text{O} < \overset{\text{CPh}}{\text{CPh}} \text{CH} >$, is obtained by heating phenylacetylenebenzoylactic acid at $150\text{--}160^\circ$ for two to three hours with fuming hydrochloric acid; also by distilling phenylacetylenebenzoylactic acid or diphenylfurfurancarboxylic acid over zinc-dust. It is insoluble in water and aqueous alkalis, but readily soluble in ether, alcohol, glacial acetic acid, benzene, and light petroleum; it crystallises from dilute alcohol in large, elongated, shining leaves or

at needles which melt at 91° and boil at $343\text{--}345^{\circ}$ without decomposition.

Ethyl α - α' -diphenylpyrroline- β -carboxylate, $\langle \begin{smallmatrix} \text{NH}\cdot\text{CPh} \\ \text{CPh}\cdot\text{CH} \end{smallmatrix} \rangle \text{C}\cdot\text{COOEt}$, is prepared by acting on ethyl phenylacetylenebenzoylacetate with alcoholic ammonia at the ordinary temperature. It is sparingly soluble in hot alcohol, ether, and benzene; more readily soluble in hot glacial acetic acid, from which it crystallises in large, yellow, shining needles or prisms melting at 217° .

α - α' -Diphenylpyrroline- β -carboxylic acid, $\langle \begin{smallmatrix} \text{NH}\cdot\text{CPh} \\ \text{CPh}\cdot\text{CH} \end{smallmatrix} \rangle \text{C}\cdot\text{COOH}$, obtained by hydrolysing the preceding compound, is readily soluble in boiling glacial acetic acid, but tolerably sparingly soluble in hot alcohol, from which it crystallises in orange-red needles melting at 261° . It sublimes with decomposition, but is not acted on by mineral acids, so that neither the acid nor the ethyl salt shows the pinewood reaction. F. S. K.

Isomerides of Tannic Acid. By H. SCHIFF (*Annalen*, **245**, 35—42).—Pyrogallalcarboxylic acid, prepared by the action of potassium hydrogen carbonate and water on pyrogallol, as described by Albrecht and Will (Abstr., 1884, 1335), melts with decomposition at $206\text{--}208^{\circ}$ if slowly heated, and at $215\text{--}220^{\circ}$ if the temperature is rapidly raised. It is converted into *dipyrogallalcarboxylic acid* by the action of phosphorus oxychloride. The new acid, $\text{C}_{14}\text{H}_{10}\text{O}_9$, is a yellow powder with an astringent taste. After moistening with alcohol, it dissolves readily in water.

The aqueous solution resembles tannic acid in its reactions, but is decomposed by boiling, yielding pyrogallol. The barium salt, $\text{Ba}(\text{C}_{14}\text{H}_9\text{O}_9)_2$, is a grey powder. The acid forms a pentacetyl-derivative, $\text{C}_{14}\text{H}_5\text{Ac}_5\text{O}_9$.

Ethyl pyrogallalcarboxylate has been described by Albrecht and Will (*loc. cit.*). The yield is increased by saturating the well-cooled alcoholic solution of pyrogallalcarboxylic acid with hydrogen chloride under pressure.

Diphloroglucinolcarboxylic acid, prepared by the action of phosphorus oxychloride on phloroglucinolcarboxylic acid, is partly decomposed by dilute sulphuric acid at 150° , and is partly converted into an anhydride resembling phlobaphene. W. C. W.

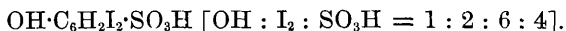
Action of Phosphorus Pentachloride on Ethyl Succinosuccinate. By S. LEVY and A. ANDREOCCHI (*Ber.*, **21**, 1463—1468).—*Dichlorodihydroterephthalic acid*, $\text{C}_6\text{H}_4\text{Cl}_2(\text{COOH})_2$, is obtained when ethyl succinosuccinate (1 mol.) is heated with phosphorus pentachloride (4 mols.) in a reflux apparatus in a water-bath until hydrogen chloride ceases to be evolved, and, after removal of the phosphorus chlorides by distillation, is separated by repeated extraction with water at 99° from a yellow compound simultaneously formed. It crystallises from water in lustrous, white scales, becomes brown at 210° , melts at $272\text{--}275^{\circ}$ with decomposition, and is readily soluble in alcohol, ether, and acetone, sparingly soluble in chloroform, benzene,

and carbon bisulphide. The *barium* salt with 3 mols. H_2O crystallises in small, pale-rose coloured prisms, and is sparingly soluble in hot water; the *calcium* salt with 4 mols. H_2O is almost insoluble in water; the *silver* salt forms small, asbestos-like needles, and is insoluble in water; and the *sodium hydrogen* salt with 3 mols. H_2O crystallises in colourless needles grouped in branch-like forms, and is very soluble in water. The *ethyl* salt, $\text{C}_6\text{H}_4\text{Cl}_2(\text{COOEt})_2$, crystallises from dilute alcohol in small, lustrous prisms, melts at $70-71^\circ$, and is readily soluble in ether, benzene, and chloroform, yielding solutions which show a bluish fluorescence; the *methyl* salt, $\text{C}_6\text{H}_4\text{Cl}_2(\text{COOMe})_2$, crystallises in thin tablets arranged in fan-like forms, and melts at $109-110^\circ$.

Paradichloroterephthalic acid, $\text{C}_6\text{H}_2\text{Cl}_2(\text{COOH})_2$, is formed from the dihydro-acid by oxidation in aqueous solution with dilute nitric acid (20 per cent.). It crystallises from water in colourless, hair-like needles, does not melt at 300° , and can be sublimed by careful heating. Its *methyl* salt melts at $131-132^\circ$. W. P. W.

Action of Alkaline Sulphinates on Trihalogen-substituted Hydrocarbons. By R. OTTO and W. OTTO (*Ber.*, **21**, 1691—1697; compare this vol., pp. 482 and 483).—Chloroform and sodium benzenesulphinate do not react when heated together in sealed tubes at 160° for eight hours. Ethylenediphenylsulphone is the chief product obtained when methylchloroform is heated with sodium benzenesulphinate at $130-140^\circ$. Benzenesulphonic acid, sodium benzenesulphonate, sodium chloride, and a small quantity of sodium sulphate are also produced. Benzylphenylsulphure is formed, together with numerous unimportant products, when benzotrichloride and sodium benzenesulphinate are heated together in alcoholic solution. F. S. K.

Iodophenolsulphonic Acids. By F. KEHRMANN (*J. pr. Chem.* [2], **37**, 334—342; compare this vol., p. 595).—When the potassium salt of the diiodophenolsulphonic acid previously described is shaken with nitric acid of sp. gr. 1.52, iodine separates, and the solution contains what is probably a dinitrophenolsulphonic acid, the potassium salt of which forms reddish-yellow crystals readily soluble in water. If, however, the iodine is filtered off and the solution boiled for a few minutes, it gives on cooling pure picric acid; hence the diiodophenolsulphonic acid must have the constitution



Di-iodoquinone, $\text{C}_6\text{H}_2\text{O}_2\text{I}_2$ [$\text{O}_2 : \text{I}_2 = 1 : 4 : 2 : 6$], is obtained when di-iodoparaphenolsulphonic acid is oxidised with chromic acid. It forms reddish-yellow scales, melts at $179-180^\circ$ (uncorr.), and sublimes readily. The corresponding quinol crystallises in colourless needles melting at $144-145^\circ$ (compare Seifert, *Abstr.*, 1884, 431).

Orthiodocresolsulphonic acid,



crystallises in large plates containing 3 mols. H_2O . The potassium and barium salts are described. With nitric acid of sp. gr. 1.52, it

yields a dinitrocresol $[\text{OH} : \text{Me} : (\text{NO}_2)_2 = 1 : 2 : 4 : 6]$ melting at $85-86^\circ$, and on oxidation with chromic acid an iodomethylquinone $[\text{Me} : \text{O}_2 : \text{I} = 2 : 1 : 4 : 6]$, crystallising in golden-red needles and melting at 115° , is obtained.

Under some circumstances when potassium orthocresolparasulphonic acid is iodated, besides the acid above described, an acid of the constitution $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{MeI} \cdot \text{SO}_3\text{H}$ $[\text{Me} : \text{OH} : \text{SO}_3\text{H} : \text{I} = 2 : 1 : 6 : 4]$ is obtained. With nitric acid of sp. gr. 1.52, it forms the dinitrocresol melting at $85-86^\circ$, but on oxidation with chromic acid suffers decomposition with liberation of iodine.

On sulphonating thymol and treating the sulphonic acid so formed with iodine, a monoiodothymolsulphonic acid is obtained, which on oxidation with chromic acid furnishes a monoiodopropylmethyl quinone, and therefore contains the sulphonic acid group in the para-position to the hydroxyl.

G. T. M.

Di-iodophenolsulphonic Acid. By F. KEHRMANN (*J. pr. Chem.* [2], 37, 359—360).—This is a controversial paper in answer to a recent one by Ostermayer (this vol., p. 596).

Splitting of the Naphthalene and Benzene Rings by Oxidation. By R. HENRIQUES (*Ber.*, 21, 1607—1620).—When an aqueous solution of sodium α -naphthoxide is treated with potassium permanganate so long as the latter is decolorised, orthocarboxylphenylglyoxylic acid, $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{COOH}$ (Zincke and Breuer, *Abstr.*, 1885, 270, and Scherks, *ibid.*, 533), is obtained, but scarcely any phthalic acid is formed, as when the oxidation takes place in acid solution. When heated with alkaline permanganate solution, phthalic acid is slowly formed. Anhydrosphenylhydrazine orthocarboxylphenylglyoxylic acid, $\text{CO} < \text{C}_5\text{H}_4 \text{N}_2\text{Ph} > \text{C} \cdot \text{COOH}$, is precipitated in yellow flakes

when a solution of the acid is warmed with phenylhydrazine hydrochloride, and crystallises in colourless needles melting at $214-215^\circ$. It is sparingly soluble in water and ether, rather readily soluble in hot alcohol and hot glacial acetic acid. Alkalis and alkaline carbonates dissolve it readily. The *methyl* salt, prepared by heating the hydrazine compound with methyl alcohol and methyl iodide, forms readily soluble needles which melt at 114° . When the free acid is heated above its melting point, it is converted into the internal anhydride, $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}$ (Racine, *Abstr.*, 1887, 951), which melts at $106-107^\circ$. This when boiled for a long time yields phthalanil.

When α -naphthol (100 grams) is oxidised with potassium permanganate (500 grams) in presence of soda (28 grams), filtered from manganese dioxide, and acidified with sulphuric acid, 95 grams of crude phthalic acid, together with an acid of the formula $\text{C}_{20}\text{H}_{14}\text{O}_8$ are obtained. The latter separates in yellow flakes on adding acid, and is purified by boiling it several times with glacial acetic acid and with alcohol. It forms a very insoluble, white powder, which melts at 246° . The *sodium* and *barium* salts are very readily soluble; the latter crystallises well. When treated with potassium permanganate in alkaline solution, it yields carboxyphenylglyoxylic acid. When

boiled with an excess of phenylhydrazine, the compound $C_{26}H_{18}N_2O_6$ is obtained. This crystallises in small needles melting at 175° with decomposition, very readily soluble in alcohol, less in benzene. When the acid $C_{20}H_{14}O_8$ is heated at its melting point, it gives off carbonic anhydride and is converted into diphthalyl and a new acid of the formula $C_{19}H_{10}O_6$; this melts at $162-163^\circ$.

If in the oxidation of α -naphthol the temperature is not kept below $35-40^\circ$, and the product after being acidified is treated with phenylhydrazine, a mixed powder is obtained containing anilphthalimide and Hötte's phenylhydrazide (Abstr., 1887, 669).

When α - and β -naphthalenesulphonic acids are oxidised with potassium permanganate, they also yield orthocarboxylphenylglyoxylic acid.

When a dilute aqueous solution of phenol is gradually treated with potassium permanganate, a considerable amount of oxalic acid is formed; when a larger amount of permanganate (330 grams to 50 grams of phenol) is used, a small quantity of salicylic acid is produced.

N. H. M.

Action of Quinonedichlorimide on β -Naphthylamine. By R. NIETZKI and R. OTTO (*Ber.*, 21, 1598—1602).—When quinone dichlorimide is added to β -naphthylamine dissolved in 5 to 6 parts of alcohol, the solution acquires an intense red colour, and on adding water the colour changes to yellow, and a separation of yellowish-brown flakes takes place. The compound so formed is a eurhodine

of the formula $C_{10}H_6 \begin{array}{c} \diagup N \diagdown \\ | \\ N \end{array} C_6H_5 \cdot NH_2$. It crystallises from benzene in

dark yellow needles, rather sparingly soluble in alcohol and benzene, readily soluble in aniline. The alcoholic solution shows a strong fluorescence. Hydrochloric and sulphuric acids dissolve it with formation of intense magenta and reddish-brown coloured solutions respectively. When the solution in 60 parts of alcohol is treated with sulphuric acid and sodium nitrite, Witt's naphthophenazine is formed.

Quinonedichlorimide reacts with phenyl- β -naphthylamine in alcoholic

solution with formation of the compound $C_{10}H_6 \begin{array}{c} \diagup N \diagdown \\ | \\ NPhCl \end{array} C_6H_5 \cdot NH_2$.

The red solution is precipitated with zinc chloride. It is purified by means of the nitrate. It forms a blue-violet precipitate soluble in alcohol and ether; the solutions are also violet and are not fluorescent. The nitrate crystallises in slender needles. The dye has a striking resemblance to that obtained by removing an amido-group from safranin. It is dissolved by strong sulphuric acid with blackish-violet colour, which changes on addition of water to a dirty green, then to orange, and finally to carmine-red.

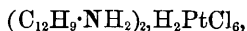
The assumption of the presence of a phenylazonium-group is supported by the fact that by the introduction of phenyl into the but feebly basic eurhodine a rather strong base is formed which yields salts not decomposed by alkaline carbonates.

N. H. M.

Nitro-derivatives of Acenaphthene. By F. QUINCKE (*Ber.*, 21, 1454—1463; compare Abstr., 1887, 592).—When acenaphthene

(80 grams) dissolved in acetic acid (1 kilo.) is treated with nitric acid (50 c.c.) free from lower oxides of nitrogen, it yields a mixture of nitracenaphthene (50 grams) and dinitracenaphthene (20 grams), from which the former can be extracted by digestion with light petroleum. *Dinitracenaphthene*, $C_{12}H_8(NO_2)_2$, crystallises in yellow needles, melts at 206° with carbonisation, and is probably identical with Berthelot's derivative obtained by the action of fuming nitric acid (*Bull. Soc. Chim.*, **8**, 250).

When reduced with tin and hydrochloric acid, nitroacenaphthene is converted into amidacenaphthene. The product, however, is not pure, since a portion is further reduced to acenaphthene, which unites with the amine to form a compound crystallising from alcohol with a constant melting point of 96° , whilst amidacenaphthene itself crystallises in needles melting at 108° . The *hydrochloride*, $C_{12}H_9 \cdot NH_2 \cdot HCl$, crystallises in slender needles; the *platinochloride*,



crystallises in deliquescent, reddish-yellow needles; the *stannoehloride*, $C_{12}H_9 \cdot NH_2 \cdot HSnCl_3$, crystallises in brownish-red, prismatic forms, and the *picrate*, $C_{12}H_9 \cdot NH_2 \cdot C_6H_2(NO_2)_3 \cdot OH$, forms yellow crystals. The *acetyl-derivative*, $C_{12}H_9 \cdot NHAc$, crystallises from alcohol in dark yellow scales, and melts at 176° ; the *diacetyl-derivative*, $C_{12}H_9 \cdot NAc_2$, crystallises from alcohol in bright brown spangles and melts at 122° ; the *benzoyl-derivative*, $C_{12}H_9 \cdot NHBz$, crystallises from alcohol in silky yellowish needles and melts at 210° ; the *thiocarbamide*, $CS(NH \cdot C_{12}H_9)_2$, crystallises from toluene in slender, pale yellow or violet, asbestos-like needles and melts at 192° , and the *thiocarbimide*, $C_{12}H_9NCS$, crystallises from alcohol in brown lustrous scales and melts at 96° .

Diamidacenaphthene is obtained from dinitracenaphthene by reduction either with tin and hydrochloric acid, or with hydriodic acid and phosphorus at 100° , but could not be separated in a pure form owing to the ease with which it decomposes. The salts are likewise very unstable; the *picrate* crystallises in yellow needles; the *hydrochloride*, $C_{12}H_8(NH_2)_2 \cdot 2HCl$, and *hydriodide*, $C_{12}H_8(NH_2)_2 \cdot 2HI$, were also prepared.

When oxidised with potassium chromate and dilute sulphuric acid, with potassium permanganate in alkaline solution, or best with nitric acid (sp. gr. = 1.2), nitracenaphthene is converted into nitronaphthalic acid and nitro- γ -naphthaquinone. A better yield, however, is obtained by heating acenaphthene (30 grams) with nitric acid of sp. gr. = 1.2 (600 c.c.) in a reflux apparatus for three hours, whereby both the acid (2 grams) and the quinone (15 grams) are formed. *Nitronaphthalic acid*, $NO_2 \cdot C_{10}H_5(COOH)_2$, crystallises in slender yellow needles, is sparingly soluble in alcohol, ether, and light petroleum, and decomposes at 140 – 150° with the formation of the *anhydride*, $NO_2 \cdot C_{10}H_5 \cdot C_2O_2 \cdot O$, which melts at 220° . The salts are readily soluble in water; the *calcium* salt, with 1 mol. H_2O , crystallises in yellow scales, and the *ammonium* salt, with 1 mol. H_2O , in yellow needles. *Nitro- γ -naphthaquinone*, $C_{10}H_5O_2 \cdot NO_2$, crystallises in yellowish-red needles, melts at 208° , and is soluble in alcohol and acetic acid. The *anilide*, $NO_2 \cdot C_{10}H_4O_2 \cdot NHPh$, crystallises in dark

violet needles, melts at 128° with decomposition, and is sparingly soluble in all the ordinary solvents except acetic acid; the *diphenylamine*-derivative, $\text{NO}_2 \cdot \text{C}_{10}\text{H}_7\text{O}_2 \cdot \text{NPh}_2$, forms green flocks, melts at 80° with decomposition, and is readily soluble in alcohol, acetic acid, and light petroleum, but sparingly soluble in ether.

W. P. W.

Molecular Refraction as a Means of Determining the Constitution of Members of the Terpene-group. By O. WALLACH (*Annalen*, **245**, 191—213).—As in some cases the terpenes which Brühl used in his research on molecular refraction (this vol., pp. 377 and 494) were impure, the author has re-determined the index of refraction with terpenes of undoubted purity with the following results:—

	n_D	$\frac{(n^2 - 1)p}{(n^2 + 2)d}$	Calculated refraction equivalent.
Cineol, $\text{C}_{10}\text{H}_{18}\text{O}$	1.4559	45.16	45.10
Terpineol, $\text{C}_{10}\text{H}_{18}\text{O}$	1.48084	46.82	46.88
Dipentene, $\text{C}_{10}\text{H}_{16}$	1.47308	45.10	45.00
Sylvestrene, $\text{C}_{10}\text{H}_{16}$	1.47468	45.08	45.00

W. C. W.

Action of Acids and Anhydrides on Terpenols. By J. LAFONT (*Compt. rend.*, **106**, 1170—1171).—Terpilenol mixed with an equivalent quantity of formic acid slowly undergoes etherification at the ordinary temperature, but the change is always far from complete. At 100° , or with equal weights of terpilenol and acid, the terpilenol splits up into water and terpineol, the latter becoming partially polymerised. With acetic acid at the ordinary temperature, terpilenol undergoes etherification very slowly, and the reaction is far from complete. At 100 — 150° the change is more rapid, and at the higher temperature it may amount to 5 per cent.

Terpilenol can, however, be readily and completely converted into the acetate, $\text{C}_{10}\text{H}_{16} \cdot \text{C}_2\text{H}_4\text{O}_2$, by heating it with a slight excess of acetic anhydride in sealed tubes at 100° for 24 hours. When treated with alcoholic potash at 100° , the acetate yields the original terpilenol.

Precisely the same results were obtained with terpilenols from two different sources.

When terpilenol from terpin is treated with aqueous chromic acid, no aldehyde and no ketone is formed, but acetic acid is obtained in small quantity and terpene is produced by dehydration. The chromic acid partially destroys the molecule. From these results it follows that terpilenols have many of the peculiarities of tertiary alcohols.

C. H. B.

Camphor from the Ethereal Oil of *Ledum Palustre*. By B. RIZZA (*J. Russ. Chem. Soc.*, 1887, 319—325).—A. Gorboff has examined the posthumous papers of B. Rizza, and in his diary finds data according to which the camphor from *Ledum palustre* has the formula $\text{C}_{15}\text{H}_{26}\text{O}$. On heating the camphor with acetic anhydride, two layers are obtained, of which the lower consists of acetic acid, whilst the upper contains a hydrocarbon of the composition $\text{C}_{15}\text{H}_{24}$, belonging to the class of sesquiterpenes (C_5H_8)₃; this is a liquid of

sp. gr. 0.9349 at 0°, and 0.9237 at 19°, and boils at 264°. It combines with bromine. The camphor is regarded by the author as a sesquiterpene hydrate. The oil of *Ledum palustre* seems to be identical with the above hydrocarbon, as after drying it distills in a current of hydrogen at 260—270°. B. B.

Hydrocarbons in Resin Oils. By A. RENARD (*Compt. rend.*, 106, 1086—1087).—That portion of resin oil which is not attacked by strong sulphuric acid yields a mixture of two hydrocarbons boiling at 330—350°, which cannot be separated by fractionation. The portion boiling at 340—350° contains diterebenthylene identical with that obtained by the action of heat on diterebenthyl dibromide. The portion boiling at 330—340° also contains diterebenthylene, but consists mainly of a new hydrocarbon; this is isolated by two or three successive treatments with sulphuric acid or with fuming nitric acid, which converts the diterebenthylene into either a sulphonic derivative soluble in water or a nitro-derivative soluble in nitric acid. The unattacked portion is washed with sodium hydroxide and rectified over sodium.

The hydrocarbon thus obtained has the composition $C_{20}H_{36}$, and is a colourless non-fluorescent oily liquid, which boils at 330—335°; sp. gr. at 12° = 0.9362; rotatory power of a column 10 cm. in length for $D = -2^\circ$. It does not alter when exposed to air, and is not affected by fuming sulphuric, nitric, or hydrochloric acid, nor by bromine at the ordinary temperature. It may be regarded as didecene, a polymeride of decene, $C_{10}H_{18}$.

From these and previous results, it appears that resin oils contain 80 per cent. of diterebenthyl, 10 per cent. of diterebenthylene, and 10 per cent. of didecene. C. H. B.

Shellac. By R. BENEDIKT and E. EHRLICH (*Monatsh.*, 9, 157—164).—When shellac, previously freed from fat by boiling with sodium carbonate, is boiled with caustic alkalis for two hours, and the cold solution acidified with sulphuric acid, about 70 per cent. of a viscous, liquid shellac is precipitated. The product is extracted with ether, and purified by means of the magnesium salt ($C_{46}H_{70}Mg_2O_{13}$). It is a thick, viscous liquid, which becomes mobile when heated, and is only very sparingly soluble in boiling water, but dissolves readily in alcohol and ether. The alcoholic solution is precipitated by water. When heated, water is evolved and on cooling a solid mass very similar to ordinary shellac is obtained. The acid value of liquid shellac is nearly three times as great as that of ordinary shellac, 1 gram requiring 0.204 gram of potash for complete saturation. From this datum and from the elementary analysis, the formula of liquid shellac is probably $C_{46}H_{72}O_{12}$. A mixture of ordinary and liquid shellac is obtained by boiling two portions of shellac, one with sodium carbonate, the other with soda, separating the wax and acidifying the cold mixed solutions with acetic acid. It is a plastic resin which when free from acid retains its plastic condition for a considerable time, but after several months gradually begins to harden at the surface. The alkaline-earth salts of liquid shellac are

soluble in cold water in all proportions, they are precipitated as thick liquids when the solution is boiled, but redissolve completely on cooling. When an aqueous solution is evaporated over sulphuric acid, a completely transparent residue is obtained, which after some time becomes opaque. These salts are very brittle, and even in the dry state are very readily soluble in cold water. The *barium* salt is obtained by neutralising an alcoholic solution with baryta-water. A solution of the magnesium salt gives with lead, silver, and zinc salts white precipitates which form resinous masses when warmed.

Shellac freed from wax yields 20 per cent. of azelaic acid when boiled with potash and potassium permanganate, products smelling like butyric acid being also formed. Shellac is completely converted into azelaic acid and fatty acids by potassium permanganate, when the residual resin is again boiled with the permanganate, and the process repeated until the whole is oxidised. F. S. K.

Apiole. By G. CIAMICIAN and P. SILBER (*Ber.*, **21**, 1621—1633).—*Iso-apiole*, $C_{12}H_{14}O_4$, is prepared by heating 25 grams of apiole with 50 grams of potash and 250 c.c. of absolute alcohol for 10 to 15 hours on a water-bath. The product is cooled, poured into 1 litre of water and filtered. The crystals are pressed between filter-paper and crystallised from alcohol. It forms large plates, melts at $55-56^\circ$, and boils at $303-304^\circ$, and is readily soluble except in water. The yield is 70 to 75 per cent.

Apiolic acid, $C_{10}H_{10}O_6$, is obtained by gradually adding a solution of 32 grams of potassium permanganate in 1600 c.c. of water to 8 grams of *iso-apiole* in 800 c.c. of boiling water containing potash. The mixture is afterwards heated in a water-bath for one hour. The yield is 37 to 38 per cent. A small quantity of apionaldehyde melting at 102° (Ginsberg, this vol., p. 722) is also formed. *Apiolic acid* crystallises from water in needles melting at 175° , soluble in ether, hot alcohol, hot glacial acetic acid, benzene, and ethyl acetate. The *silver salt*, $C_{10}H_9AgO_6$, crystallises in large needles, the *calcium salt* in prisms of a glassy lustre. The *methyl salt* melts at $71-72^\circ$, and dissolves in ether, alcohol, and glacial acetic acid, sparingly in hot water. The same acid is formed in small quantity in the oxidation of apiole with potassium permanganate, the chief product being a neutral compound of the formula $C_{12}H_{16}O_6$ (this vol., p. 606).

Apionaldehyde, $C_{10}H_{10}O_5$, (Ginsberg, *loc. cit.*) is prepared by gradually treating 2 grams of *iso-apiole* with a mixture of 10 grams of potassium dichromate with 200 grams of dilute sulphuric acid (1 : 10) and boiling for three hours. It is then steam-distilled to remove acetaldehyde and acetic acid, which are also formed, filtered, and the crystals which separate on cooling crystallised from alcohol. It is readily purified by means of the *hydrogen sodium sulphite compound*. The aldehyde can be obtained from apiole but the yield is not at all good. The *oxime*, $C_{10}H_{10}O_4 \cdot N \cdot OH$, crystallises in long needles, melts at $160-161^\circ$, dissolves sparingly in hot water, readily in ether, hot alcohol, and acetic acid; it dissolves in sulphuric acid with yellow colour which changes to olive-green when the solution is slightly warmed.

When apiolaldehyde is oxidised with permanganate, apiolic acid melting at 175° is formed almost quantitatively. When apiolaldehyde (1 gram) is dissolved in glacial acetic acid (10 c.c.), and treated with cold nitric acid (sp. gr. 1.35, 40 grams), a *nitro-derivative*, $C_7H_7NO_5$, is obtained. This crystallises from alcohol in yellow needles which melt at $137-138^{\circ}$.

When apiolic acid is heated with dilute sulphuric acid at 140° for five hours, it is converted into *apione*, $C_9H_{10}O_4$, and carbonic anhydride. The product is steam-distilled, and the slender, white needles so obtained crystallised from alcohol. It melts at 79° , dissolves readily in ether, acetic acid, and boiling alcohol, and is insoluble in water.

A bromine-derivative, probably *dibromapione*, is formed when apiolic acid or the aldehyde is treated with bromine. It melts at $99-100^{\circ}$.

The physiological properties of iso-apiole and of apiole are described. N. H. M.

Picrotoxin. By B. v. D. MARCK (*Arch. Pharm.* [3], 26, 269, from *Nieuw. Tijdsch. Pharm. Nederland.*, 1888, 25).—In opposition to the views of others, the author recommends light petroleum for the extraction of picrotoxin from the pulverised fruit of *Anamista coccula*. On distilling off the solvent, a crystalline product is obtained, soluble in acidified water, with the exception of some chlorophyll and resin. The filtrate on evaporation, gives the picrotoxin in pale-yellowish crystals, which by repeated recrystallisation become snow-white.

J. T.

Ophioxylin. By W. BETTINK (*Arch. Pharm.* [3], 26, 268—269, from *Nieuw. Tijdschr. Pharm. Nederland.*, 1888, 1).—This crystallisable compound, obtained from the root of *Ophioxylon serpentinum*, forms orange-yellow crystals of the tetragonal system; it has a sharp, burning taste, is sparingly soluble in water, more soluble in alcohol, and very soluble in chloroform, benzene, and carbon bisulphide. Its elementary analysis gives the formula $C_{16}H_{15}O_6$ or $C_{48}H_{39}O_{18}$. In most of its properties and reactions, it agrees with juglone, but it melts at 71.8° , whilst juglone melts at $151-154^{\circ}$.

J. T.

Crystalline Arrow-poison of the Comalis, extracted from the Wood of the Ouabaïo.—By ARNAUD (*Compt. rend.*, 106, 1011—1014).—The Comalis on the East Coast of Africa prepare an arrow-poison from the aqueous extract of the wood, and especially of the root of the Ouabaïo, a tree which is closely related to although not identical with *Carissa schimperi*, a native of Abyssinia.

A concentrated extract of the wood in warm water was prepared and precipitated with lead acetate, the filtrate treated with hydrogen sulphide, and the second filtrate boiled and afterwards concentrated in a vacuum. The concentrated solution was mixed with six times its volume of alcohol of 85° , boiled, allowed to cool in shallow vessels, and the crystals thus obtained purified by recrystallisation first from alcohol of 85° and afterwards from water.

The *ouabain* thus obtained contains no nitrogen and has the composition $C_{30}H_{46}O_{12}$. It forms thin, white, nacreous lamellæ with no

taste, no smell, and a neutral reaction. It is almost insoluble in cold water, but is readily soluble in boiling water, with a great tendency to form supersaturated solutions, and also dissolves readily in moderately concentrated alcohol, but is almost insoluble in absolute alcohol and insoluble in ether or chloroform. At 180° , it becomes pasty with slight decomposition, and at 200° it is completely melted. A warm aqueous solution has a rotatory power $[\alpha]_D = -34^{\circ}$. A concentrated aqueous solution gives a precipitate with tannin. When boiled with dilute acids, it yields a reducing sugar, and hence it would seem that ouabain is a glucoside.

When ouabain crystallises from an aqueous solution, it contains 7 mols. H_2O which is not completely expelled below 130° .

When boiled with barium hydroxide, ouabain yields a barium-derivative which when dried at 100° has the composition $Ba(C_{30}H_{47}O_{13})_2$.

Ouabain has no toxic effect when introduced into the stomach, but when introduced by subcutaneous or intravenous injection, it acts on the heart and produces death. 2 mgrams. will kill a dog of 12 kilos. in a few minutes.

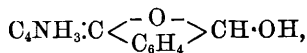
C. H. B.

Bases Formed by the Action of Hydrochloric Acid on Pyrrolines. By M. DENNSTEDT and J. ZIMMERMANN (*Ber.*, 21, 1478—1481).—The hydrochloride of a base which is obtained when hydrochloric acid is passed into an ethereal solution of pyrroline (*Abstr.*, 1887, 598) has the formula $(C_4NH_5)_3.HCl$. It is soluble in water and alcohol, but cannot be crystallised from either solvent. The *platinochloride* and *picrate* are both unstable. Potassium chromate, ferrocyanide and ferricyanide give brown, amorphous precipitates. The sparingly soluble *hydriodide* is precipitated in white crystals by adding potassium iodide, and the free base $(C_4NH_5)_3$ is obtained in the form of a white, amorphous precipitate on adding ammonia to an aqueous solution of the hydrochloride. The base is decomposed not only when heated at a relatively low temperature, but also when heated with methyl iodide, or when boiled with acetic anhydride and sodium acetate.

The crystalline salt obtained when hydrochloric acid is passed into an ethereal solution of isopropylpyrroline (*loc. cit.*) has the formula $(C_7NH_{11})_2.HCl$. The *picrate*, $(C_7NH_{11})_2.C_6H_3N_3O_7$, crystallises from alcohol in long, brown, shining needles melting at 146° . The free base is a heavy, slightly yellow oil which boils at 285 — 290° and smells something like turpentine. When heated quickly, it can be distilled with partial decomposition, and on exposure to the air it is gradually converted into the isomeric isopropylpyrroline.

F. S. K.

Reduction of Pyrrolinephthalide. By M. DENNSTEDT and J. ZIMMERMANN (*Ber.*, 21, 1554—1556).—*Pyrrolinephthalide*,



is prepared by gradually adding 8 per cent. sodium amalgam to 2 to 3 grams of finely powdered pyrrolinephthalide suspended in 250 c.c. of water; after two to three days, it is filtered through asbestos, very

slightly acidified with quite dilute sulphuric acid and several times quickly extracted with ether. It crystallises from alcohol in needles melting at 118° , and is readily soluble in the usual solvents. The crystals as well as the solutions of the substance soon become reddish or green. When the ethereal solution is evaporated very gradually, well-formed, lustrous, rhombohedro-tetartohedric prisms are obtained; $a:c = 1:0.8491$. The *silver salt* is an unstable, reddish, crystalline substance, which when dried, even in the dark, decomposes with explosive violence. N. H. M.

Action of Pyridine on Metallic Salts. By W. LIANG (*Ber.*, 21, 1578—1588).—*Zinc chloride pyridine*, $\text{ZnCl}_2 \cdot 2\text{C}_5\text{NH}_5$, is prepared by treating an aqueous solution of zinc chloride with an excess of pyridine, when it separates as a voluminous, white precipitate; its formation is accompanied by development of heat. It crystallises from water in long, white needles of a silky lustre which consist of fibrous aggregates. When washed or boiled repeatedly with fresh quantities of water, it decomposes with liberation of pyridine and formation of a basic zinc chloride. If the same water is used, the decomposition is limited. The compound is rather stable when exposed to air, and is only slowly decomposed at 130° to 160° . It is possible to free alcohol from pyridine which it may contain by adding zinc chloride. The *hydrochloride*, $\text{ZnCl}_2 \cdot 2\text{C}_5\text{NH}_5(\text{HCl})_2$, forms groups of white, lustrous needles.

Cupric chloride pyridine, $\text{CuCl}_2 \cdot 2\text{C}_5\text{NH}_5$, is precipitated in splendid greenish-needles of a silky lustre, when pyridine is added to an alcoholic solution of cupric chloride. It is soluble in pyridine, in water containing pyridine, and in aqueous ammonia; it is decomposed by water, but only so long as the amount of pyridine liberated does not reach a certain point. At the ordinary temperature it is stable and loses only traces of pyridine when heated at 100° ; it melts at 180 — 190° . The *hydrochloride* crystallises from water in dark-yellow prisms.

Cupric sulphate pyridine, $\text{CuSO}_4 \cdot \text{C}_5\text{NH}_5 + 3\text{H}_2\text{O}$, crystallises in sky-blue needles of silky lustre; when heated at 100° , it gives up water without losing its lustre; the anhydrous salt, probably identical with that obtained by Jörgensen (*Abstr.*, 1886, 857), recovers its blue colour when exposed to air.

Cuprous chloride pyridine, $\text{Cu}_2\text{Cl}_2 \cdot 4\text{C}_5\text{NH}_5$, obtained by adding solid cuprous chloride to pyridine, crystallises in greenish-gold-coloured, transparent octahedra, which quickly decompose when exposed to air. When a large excess of pyridine is used, the compound $\text{Cu}_2\text{Cl}_2 \cdot 6\text{C}_5\text{NH}_5$ separates in long, greenish-yellow, transparent needles which lose pyridine more quickly than the regular crystals. The solution absorbs carbon monoxide just as readily as ammoniacal cuprous chloride solution.

Cadmium chloride pyridine, $\text{CdCl}_2 \cdot 2\text{C}_5\text{NH}_5$, crystallises from water (which decomposes it partly) in needles.

Cadmium iodide pyridine, $\text{CdI}_2 \cdot 2\text{C}_5\text{NH}_5$, forms long, white needles of a silky lustre.

A table is given showing the amount of pyridine lost by the above compounds at temperatures varying from 100° to 160° .

Mercuric chloride pyridine, $\text{HgCl}_2 \cdot \text{C}_5\text{NH}_5$, is rather readily decomposed by water; it is stable when exposed to air, but is decomposed at 100° .

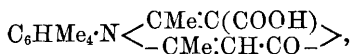
With mercurous salts, no derivatives could be obtained; mercury separates and the mercuric compounds are formed.

Calcium chloride pyridine, $\text{CaCl}_2 \cdot 3\text{C}_5\text{NH}_5$, is a loose, white powder. Compounds of pyridine with cobaltous chloride, ferrous sulphate, and nickel sulphate are also described. N. H. M.

Condensation of Ethyl Tetramethylphenylamidocrotonate.

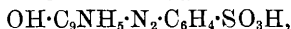
By M. CONRAD and L. LIMPACH (*Ber.*, **21**, 1655—1657).—*Ethyl tetramethylphenylamidocrotonate*, $\text{C}_6\text{HMe}_4\text{NH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{COOEt}$, is obtained by the action of tetramethylamidobenzene [$\text{NH}_2 : \text{Me}_4 = 1 : 2 : 3 : 4 : 6$], prepared from pseudocumidine (Nölting and Baumann, *Abstr.*, 1885, 893; compare also Limpach, this vol., p. 464) on ethyl acetoacetate. After two days, the solid portion of the product is crystallised from ether and alcohol. It forms large, white prisms, melting at 101° .

Tetramethylphenyllutidoncarboxylic acid,



is formed (as ethyl salt) together with tetramethylamidobenzene and ethyl alcohol when ethyl tetramethylphenylamidocrotonate is heated for some minutes at 280 — 285° . The product is heated in a reflux apparatus with alcoholic potash. The acid is readily soluble in alcohol and ether, melts at 145° and decomposes carbonates. N. H. M.

Azo-dyes of the Hydroxyquinolines. By J. MATHEÛS (*Ber.*, **21**, 1642—1647).—*Benzeneazoparahydroxyquinolinesulphonic acid*,



prepared from diazobenzene sulphochloride and parahydroxyquinoline, crystallises in small, orange-red needles, soluble in hot water and cold dilute alkali. The *sodium salt* forms red needles.

Benzeneazoparahydroxyquinoline, $\text{OH}\cdot\text{C}_9\text{NH}_5\cdot\text{N}_2\cdot\text{Ph}$, obtained from diazobenzene chloride and parahydroxyquinoline, crystallises from absolute alcohol in long, orange-red needles, soluble in ether and benzene, insoluble in water; the *sodium salt* forms red needles.

Paratolueneazoparahydroxyquinoline, $\text{OH}\cdot\text{C}_9\text{NH}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Me}$, from diazoparatoluene chloride, crystallises from alcohol in wide, red needles, soluble in ether and benzene. The *sodium salt* forms dark-red needles.

Parabromobenzeneazoparahydroxyquinoline, $\text{OH}\cdot\text{C}_9\text{NH}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Br}$, crystallises from chloroform in bright-red, matted needles. It dissolves sparingly in alcohol, readily in chloroform and in alcoholic soda.

β -Naphthaleneazoparahydroxyquinoline, $\text{OH}\cdot\text{C}_9\text{NH}_5\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_7$, crystallises from absolute alcohol in small, dark-red needles. The *sodium salt* has a still darker red colour.

Benzeneazo-orthohydroxyquinoline, $\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}$, crystallises from alcohol in long, brownish-yellow, lustrous needles, soluble in ether, in chloroform, and in alcoholic potash. The *sodium salt* is yellowish-brown.

Paratolueneazo-orthohydroxyquinoline, $C_{15}H_{13}N_3O$, crystallises from chloroform in yellowish-brown plates of a metallic lustre.

Parabromobenzeneazo-orthohydroxyquinoline, $C_{15}H_{10}BrN_3O$, is precipitated by hydrochloric acid from its solution in alcoholic soda in slender, gold-coloured needles soluble in absolute alcohol and ether.

β -Naphthaleneazo-orthohydroxyquinoline, $OH \cdot C_9NH_5 \cdot N_2 \cdot C_{10}H_7$, forms reddish-brown needles, soluble in ether, absolute alcohol, chloroform, and alcoholic soda.

Amidoparahydroxyquinoline, $OH \cdot C_9NH_5 \cdot NH_2$, is formed together with sulphanic acid when a mixture of benzeneazoparahydroxyquinoline-sulphonic acid and an excess of stannous chloride is treated with hydrochloric acid. It is purified by carefully neutralising the rather concentrated solution of the hydrochloride with solid sodium carbonate, when the free base separates in slender needles which are dried on tiles. It dissolves readily in absolute alcohol, sparingly in ether, benzene, and chloroform. Alkali solutions dissolve it readily with a green colour which quickly changes to brown. It crystallises from water with 2 mols. H_2O . The hydrochloride forms red prisms readily soluble in water; the sulphate crystallises in reddish-yellow prisms soluble in hot water; the *picrate* separates from its alcoholic solution in dark-red plates; the stannochloride forms lustrous, yellow plates, readily soluble in cold water. (Compare Abstr., 1884, 1370.)

N. H. M.

Lepidine-derivatives. By B. HEYMANN and W. KOENIGS (*Ber.*, **21**, 1424—1430).—When lepidine [$Me = 4'$] is treated with benzaldehyde and zinc chloride, it is converted into benzylidenelepidine, which is reduced to *benzyllepidine*, $C_9NH_6 \cdot CH_2 \cdot CH_2Ph$, by boiling for 10 hours with a mixture of acetic acid, amorphous phosphorus, and hydriodic acid (saturated at 0°). This crystallises well from alcohol and light petroleum, and melts at 100 — 101° .

Parahydroxybenzylidenelepidine,



is obtained by heating lepidine (2 grams) with parahydroxybenzaldehyde (1.7 grams), and finely powdered potassium hydrogen sulphate (5 grams) at 150 — 160° for eight hours. It crystallises from absolute alcohol in anhydrous, yellow needles or prisms, melts at 252 — 253° , and is sparingly soluble in dilute aqueous soda. Its *hydrochloride* crystallises in fiery-red needles, and is sparingly soluble in alcohol and water. On reduction, the base yields *parahydroxybenzyllepidine*, $C_9NH_6 \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot OH$, which melts at 179 — 180° , is crystalline, and closely resembles homo-apocinchine (this vol., p. 72) in its solubility, melting point, and crystalline appearance: the hydrobromides of the two bases also crystallise in similar forms, and show a like solubility in water, but the hydrobromide of the former melts at about 250° , whereas that of the latter melts at 220 — 222° . The crystals of the two bases could not be obtained in a suitable form for crystallographic measurement.

Orthohydroxybenzylidenelepidine,



prepared in like manner from orthohydroxybenzaldehyde, crystallises in slender, yellow forms, melts at 219° , and dissolves more readily in alcohol than the para-compound. The *hydrochloride* is a reddish-yellow salt, and is sparingly soluble in water and alcohol.

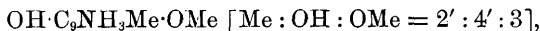
Metanitrobenzylidenelepidine, $C_9NH_8 \cdot CH : CH \cdot C_6H_4 \cdot NO_2$ [$CH : NO_2 = 1 : 3$], is obtained by heating lepidine (2 grams) with metanitrobenzaldehyde (2.1 grams) and potassium hydrogen sulphate (5 grams) at $150-160^{\circ}$ for eight hours. It crystallises from alcohol in pale greenish-yellow, concentrically grouped needles, melts at $135-136^{\circ}$, and is sparingly soluble in cold alcohol. The *hydrochloride* forms yellow flocks, and is very sparingly soluble in water and alcohol.

Benzylquinabine, $C_9NH_8 \cdot CH_2 \cdot CH_2Ph$, obtained from quinaldine by a method similar to that employed for the preparation of benzylepidine, forms colourless crystals, melts at 30° , and is readily soluble in benzene and light petroleum. The *picrate* crystallises in bright yellow prisms, melts at 130° , and is sparingly soluble in hot alcohol.

W. P. W.

Synthesis of Dihydroxyquinaldine-derivatives. By M. CONRAD and L. LIMPACH (*Ber.*, **21**, 1649—1654).—*Ethyl paramethoxyphenylamidocrotonate*, $C_{13}H_{17}NO_3$, is prepared by mixing an ethereal solution of paranisidine (m. p. 56°) with ethyl acetoacetate. After 24 to 28 hours, the ether is evaporated off, and the ethyl salt remains as a crystalline mass. It crystallises from alcohol in large prisms melting at 46° .

Paramethoxy- γ -hydroxyquinaldine,



is obtained by heating the above ethyl salt for a few minutes at 260° ; the yield is 37 per cent. of the theoretical. When heated quickly, it melts at 290° with only slight decomposition. It is sparingly soluble in boiling water. The *hydrochloride* crystallises in long needles, readily soluble in hot water; the *platinochloride* forms long, lustrous, orange-yellow prisms readily soluble in hot water; the *sulphate* crystallises in needles soluble in about 170 parts of cold water.

Paramethoxy- γ -chloroquinaldine, $C_{11}H_{10}NOCl$, is prepared by heating the dry hydroxy-derivative with twice the amount of phosphorus oxychloride in a reflux apparatus first at 100° and afterwards at 140° , as long as hydrogen chloride is evolved. The product is poured into water, treated with sodium carbonate, and extracted with ether. It forms white prisms, of a silky lustre, insoluble in water, readily soluble in dilute acids, alcohol, ether, and benzene. It melts at 100° and distils at $295-302^{\circ}$ without decomposition.

Para- γ -dimethoxyquinaldine, $C_9NH_4Me(OMe)_2$, obtained by heating the chloro-compound with sodium methoxide and methyl alcohol for two hours at $130-140^{\circ}$ crystallises in needles or prisms melting at 94° ; it is readily soluble in ether, alcohol, and in hot benzene, insoluble in water.

When the sodium compound of paramethoxy- γ -hydroxyquinaldine is heated with methyl iodide and benzene at $144-160^{\circ}$ for three hours, and the methyl iodide derivative so obtained is digested with freshly precipitated silver oxide, *paramethoxymethylquinaldine*, $C_{12}H_{13}NO_2$, corresponding with methylquinaldine (*Abstr.*, 1887, 680), is formed.

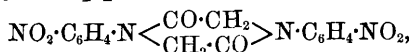
This crystallises in slender, lustrous needles, melts at 149° , and dissolves readily in boiling ethyl acetate, benzene, and alcohol, sparingly in ether; hot water dissolves it in all proportions.

Paramethoxy- γ -hydroxyquinaldine methochloride, $C_{11}H_{11}NO_2 \cdot MeCl$, crystallises in long, lustrous, white needles melting at 251° . The *platinochloride*, $(C_{12}H_{11}NO_2)_2 \cdot PtCl_6 + 4H_2O$, forms yellow needles.

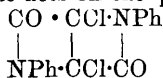
Orthomethoxy- γ -hydroxyquinaldine, $C_{11}H_{11}NO_2 + H_2O$, is prepared in a manner exactly similar to the para-compound; dianisylcarbamide, melting at 182° (not 174° , Mühlhäuser, Abstr., 1882, 302), is formed in the reaction. It crystallises in long, matted needles of a silky lustre; the anhydrous compound melts at 229° . The *platinochloride* crystallises from chloroform in lustrous, reddish-yellow plates which melt with decomposition at 239° . N. H. M.

Aromatic Halogen Acetamido-compounds and their Derivatives. By P. W. ABENIUS (*Ber.*, 21, 1665—1668).—*Diphenyldiketopiperazine*, $NPh \langle \begin{smallmatrix} CO \cdot CH_2 \\ CH_2 \cdot CO \end{smallmatrix} \rangle NPh$, crystallising in slender, white needles which melt at 263° , is obtained from brom- or chlor-acetanilide by the method already described (this vol., p. 824), or by heating chloracetylphenylglycine, $CH_2Cl \cdot CO \cdot NPh \cdot CH_2 \cdot COOH$, with aniline at 140 — 150° . *Chloroacetylphenylglycine* crystallises in plates melting at 132 — 133° .

Dinitrodiphenyldiketopiperazine,



is very sparingly soluble, and melts at a temperature too high to be accurately determined. The *amido-compound* crystallises in small, rhombic plates. When diphenyldiketopiperazine is boiled with alcoholic potash or with fuming hydrochloric acid, *phenylglycinyphenylglycine*, $NHPh \cdot CH_2 \cdot CO \cdot NPh \cdot CH_2 \cdot COOH$, melting at 129 — 130° , is formed. Phosphorous pentachloride acts on the piperazine-derivative with formation of the compound



This crystallises from alcohol with 1 mol. EtHO, in prisms melting at 247° .

Diparatolyldiketopiperazine, $C_6H_4Me \cdot N \langle \begin{smallmatrix} CO \cdot CH_2 \\ CH_2 \cdot CO \end{smallmatrix} \rangle N \cdot C_6H_4Me$ [$N : Me = 1 : 4$], is obtained together with *ethylglycolparatoluide*,



which crystallises in large, lustrous prisms melting at 32° , by the action of alcohol on bromacetoparatoluide (m. p. 164°). It is also formed by heating paratolyglycine at 200° . It crystallises in slender prisms melting at 252 — 253° .

Bromacetoparaxyldine, $C_6H_3Me_2 \cdot NH \cdot CO \cdot CH_2Br$, crystallises in needles melting at 145° .

Diparaxyldiketopiperazine, $C_6H_3Me_2 \cdot N \langle \begin{smallmatrix} CO \cdot CH_2 \\ CH_2 \cdot CO \end{smallmatrix} \rangle N \cdot C_6H_3Me_2$ [$N : Me_2 = 3 : 1 : 4$], melts at 203° .

Ethyl metamidocumate, $NH_2 \cdot C_6H_3Pr \cdot COOEt$ [$= 3 : 4 : 1$], melts at

51—52°. The *bromacetyl-derivative*, $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Pr}\cdot\text{COOEt}$, melts at 106—107°. When the latter is boiled with alcoholic potash, the *acid* $\text{COOH}\cdot\text{C}_6\text{H}_3\text{Pr}\cdot\text{N}<\begin{smallmatrix} \text{CO}\cdot\text{CH}_3 \\ \text{CH}_2\cdot\text{CO} \end{smallmatrix}>\text{N}\cdot\text{C}_6\text{H}_3\text{Pr}\cdot\text{COOH}$ is formed; this does not melt when heated: the *ethyl salt* melts at 187—188°.

N. H. M.

Morphine Hydriodide. By H. KUNZ (*Arch. Pharm.* [3], 26, 307—311).—A concentrated alcoholic solution of potassium iodide mixed with a concentrated solution of morphine hydrochloride quickly becomes a compact, crystalline mass of morphine hydriodide in hair-like needles which only slowly dissolve on the addition of more spirit. The compound was found to be $\text{C}_{17}\text{H}_{19}\text{NO}_3\cdot\text{HI} + \text{H}_2\text{O}$. Morphine hydrobromide can be similarly produced.

J. T.

Atropine and Hyoscyamine. By W. WILL (*Ber.*, 21, 1717—1726).—Hyoscyamine forms a series of crystalline salts. The *sulphate* $(\text{C}_{17}\text{H}_{23}\text{NO}_3)_2\cdot\text{H}_2\text{SO}_4$, crystallises from alcohol in slender, colourless needles melting at 206°. The *aurochloride* melts at 162°. The *hydrobromide* crystallises from water in compact prisms. The specific power of the base was found to be $[\alpha]_D = -20.97$. Hyoscyamine is converted into atropine when it is heated for five hours at 109—110°, or when a trace of soda is added to an alcoholic solution, and the whole allowed to remain for some time. Ammonia acts similarly, but only very slowly.

F. S. K.

Wrightine (Conessine) and Oxywrightine. By H. WARNECKE (*Arch. Pharm.* [3], 26, 248—261, 281—292; compare *Abstr.*, 1886, 372).—Powdered seeds of *Wrightia antidysenterica* are freed from fat by means of ether; the powder is then digested with alcohol and hydrochloric acid at 60°, freed from alcohol by distillation and digestion with water, and concentrated ammonia is added in large excess. The precipitate is washed, pressed, rubbed up with sand, and extracted with light petroleum. The almost colourless solution is shaken up with solid potash to remove all water and allowed to evaporate; and the crystalline residue is purified by recrystallisation. The formula of wrightine is probably $\text{C}_{24}\text{H}_{40}\text{N}_2$; its platinochloride, hydrochloride, nitrate, and oxalate are described; its reactions in strong hydrochloric acid solution with alkaloid reagents are also described in detail.

Oxywrightine is prepared by dissolving wrightine in 5 per cent. sulphuric acid and mixing this with dilute potassium iodate solution. After remaining 24 hours in the dark, the separated iodine is removed by chloroform and the colourless liquid is carefully treated with ammonia; after a short time a crystalline precipitate begins to form, and precipitation is rapidly completed on the addition of concentrated ammonia. The crystals of oxywrightine are anhydrous, colourless, compact needles of strongly alkaline reaction and bitter taste. This alkaloid, like atropine and hyoscyamine, strongly reddens phenolphthalein, whilst wrightine is much less effective, and the other alkaloids have still less action. Oxywrightine has the composition $4\text{C}_{12}\text{H}_{21}\text{NO}\cdot\text{C}_{12}\text{H}_{19}\text{NO}_2$.

There are also described oxywrightine platinochloride, methyl hydroxide, methochloride, and methyl hydroxide and platinochloride.

The colourless solution of oxywrightine in eight drops of concentrated sulphuric acid when heated to 90—100° becomes yellow, passing gradually to violet-red; with two drops of sulphuric acid the yellow becomes an intense rose colour. This is characteristic, and clearly shows $\frac{1}{1000}$ mgrm. J. T.

Alkaloïds of *Scopolia Japonica*. By E. SCHMIDT and H. HENSCHKE (*Arch. Pharm.* [3], 26, 185—203).—10 kilos. of scopolia root was extracted with 90 per cent. alcohol; the filtered extract, when freed from alcohol and concentrated, deposited a granulo-crystalline fatty compound whose nature was investigated by Henschke. This substance was removed and the liquid was mixed with excess of potassium carbonate solution, when a bluish phosphorescence and odour of trimethylamine made their appearance. The alkaloïds were now removed by means of chloroform, the latter distilled off at the lowest possible temperature with the aid of water, acidified with sulphuric acid, and potassium carbonate in very light excess was added to precipitate the former. Farther treatment with chloroform was necessary to remove potassium sulphate and purify the alkaloïds, but it was found impossible to obtain them in crystalline form, even on treatment with ether; a brownish syrup only resulted. To evaporate the alkaloïds, this syrup, dissolved in hydrochloric acid, was fractionally precipitated by gold chloride as suggested by Ladenburg. After repeated recrystallisation, hyoscine aurochloride, melting at 198—200°; hyoscyamine aurochloride, melting at 159—160°, and atropine aurochloride, melting at 136—138°, were isolated. J. T.

Alkaloïds of *Scopolia Hlarnackiana*. By E. SCHMIDT (*Arch. Pharm.* [3], 26, 214—215).—The freshly gathered root of this plant was examined for alkaloïds by the method employed for *Scopolia japonica*. Hyoscyamine aurochloride was the only salt obtained. The alcoholic extract showed a blue fluorescence like that obtained from *japonica*, but there was not sufficient material available to ascertain whether this was due to the presence of scopoletin. J. T.

Application of Dialysis to the Study of the Gelatinous State of Albuminoid Substances. By A. SOLOVIEFF (*J. Russ. Chem. Soc.*, 1887, 393—397).—Solutions of albuminoid substances, after removal of the gelatinous coagulum, were subjected to the dialytic action of reagents by which they are gelatinised, and in this way the observations of the time of reaction as regards the penetration of the reagents (acids or bases) into the solutions of albumin, separated from them by a membrane, could be substituted for the measurement of the weight or volume of the reagents necessary to produce the same action. From white of eggs, gelatinous coagula are obtained by the action of organic acids or mineral bases, and the action is shown to be dependent on the strength both of the reagents and of the solutions acted on. The resistance which solutions offer to the conversion of albumin into the gelatinous form may be overcome even after the

action of the reagent has taken place through the membrane, by the action of substances which are capable of withdrawing water, such as alcohols, salts, &c. The conditions of their conversion into the gelatinous state are not dependent on any deep-seated change in the structure of the albumins. For example, if albumin is boiled with hydrochloric acid of 0.2 per cent. no coagulation takes place, although after concentration it will give gelatinous coagula, whereas the same solution after the reagent has been separated by dialysis is coagulated by boiling. The method of dialysis has the advantage that not only in the case of the action of organic acids, but also in that of strong bases, the albumin is gelatinised if the dialysis is stopped at the right time. The remaining part of the paper treats on the different states of albumin (especially Tarchanoff's "tata-albumin") and their mutual conversions and relations. B. B.

Silk. By T. WEYL (*Ber.*, **21**, 1407—1410).—The author finds that when commercial discharged silk completely deprived of silk-glue by digestion with 5 per cent. aqueous soda, is washed with 5 per cent. hydrochloric acid and finally with water (compare Staedler, *Annalen*, **111**, 12), and dried at 100°, it dissolves readily in cold fuming hydrochloric acid (sp. gr. = 1.2), and that the filtered solution when poured into a large quantity of cold 90 per cent. alcohol (400 c.c. to 5 grams of silk employed) yields a very voluminous, flocculent precipitate which rapidly forms a transparent, gelatinous mass. This compound, *sericoïn*, is obtained as a white powder by washing the precipitate with alcohol, boiling it first with absolute alcohol to completely dry it, then with dry ether, and finally allowing it to remain over sulphuric acid in a vacuum. So far as the percentage of carbon and hydrogen is concerned, *sericoïn* does not differ appreciably in composition from fibroïn, but it contains about 2 per cent. less of nitrogen. *Sericoïn*, even in very concentrated solution, is optically inactive, and when boiled for some time with dilute sulphuric acid yields, like fibroïn, a substance which gives the biuret reaction with copper sulphate and dilute aqueous soda. Fuchsin and picric acid colour *sericoïn* very slightly, but Millon's reagent gives with it a red colour as with fibroïn. Inasmuch as fibroïn is nothing more than discharged silk there is nothing to show that it has yet been obtained pure, and therefore *sericoïn* may be simply purified fibroïn; ammonium chloride has, however, been detected in the acid filtrate from *sericoïn*, and this would seem to point to the elimination of some of the nitrogen in fibroïn by the action of hydrochloric acid. W. P. W.

Silk. By T. WEYL (*Ber.*, **21**, 1529—1532; compare preceding Abstract).—When white silk, purified by Städeler's method, is boiled for 18 hours with sulphuric acid (1 : 5), the biuret reaction, which is clearly shown during the first 10 hours, disappears, and the whole dissolves to a yellowish-brown liquid on the surface of which a small quantity of a fatty acid swims in the form of oily drops. Tyrosine (5.2 per cent.) crystallises from the solution after removing the sulphuric acid by means of baryta-water. The filtrate from the tyrosine yields on evaporation a crystalline mass (15 per cent.) which

is most probably α -alanine. This compound crystallises in large, seemingly rhombic prisms, is tolerably readily soluble in cold water, ammonia, and soda, but is only very sparingly soluble in 40 per cent. alcohol and insoluble in ether. An aqueous solution is not precipitated by mercuric nitrate, and does not evolve ammonia when boiled with soda. The aqueous solution is optically inactive. When heated carefully, it sublimes in woolly flocks, and on further heating an oily, basic-smelling substance separates. When heated in a capillary tube, it remains unchanged at 230°, turns brown at about 237°, and at about 255° is converted into a brown, partly oily mass. Synthetical α -alanine has the same crystalline form, and behaves similarly when heated.

Glycocine (7.5 per cent.) was isolated from the mother-liquor from the alanine. F. S. K.

Alkali and Acid Albumin-derivatives. By M. SAVIN (*J. Russ. Chem. Soc.*, 1887, 398—402).—The following are the results of the author's investigation. The so-called ammonia-albuminate of white of eggs, and the acid albumin obtained by the action of hydrochloric acid of 0.2 per cent. after precipitation with ammonium sulphate and subsequent dialysis until all salt is removed and the reaction is neutral, are insoluble in water but soluble in acids and alkalis. The solubility in salt solutions depends on the time which has elapsed since their preparation. When the dilute albumin solutions are made alkaline and then digested on the water-bath with ammonia or with soda, the albumin is converted into globulin, but the conversion is incomplete. As regards their behaviour towards water, solvents, and reagents, the acid albumins are identical with the feebly alkaline derivatives of albumin (globulins) when in the form of pure precipitates. The same holds good with regard to ferments. The fact that globulins are obtained by "tryptonisation" seems to confirm the identity of globulins with albumins. B. B.

Spectrum of Acid Methæmoglobin. By H. BERTIN-SANS (*Compt. rend.*, 106, 1243—1245).—Considerable uncertainty exists as to the number of bands in the spectrum of acid methæmoglobin, some observers holding that the two bands between E and D are due to the presence of oxyhæmoglobin. The author finds that these bands are always present whatever the proportion of reagent used to convert the oxyhæmoglobin into methæmoglobin, and they only disappear when the solution is largely diluted. Moreover, the two bands are different in character and position from the bands of hæmoglobin. If potassium ferricyanide is added to a solution of carboxyhæmoglobin the spectrum of the solution is identical with that of methæmoglobin, and if the liquid is now treated with ammonia and ammonium sulphide the spectrum of carboxyhæmoglobin reappears.

The spectrum of acid methæmoglobin consists of four bands, the mean wave-lengths being 6330, 5800, 5385, and 5000 respectively. The first is the most intense; the second is about the same breadth, but is very feeble; the third is more intense than the second, and is about twice as broad; the fourth is seen only in a dilute solution, and is broader and more intense than either the second or third. This

spectrum has a general resemblance to the spectrum of hæmatin in an acidified alcoholic solution, but is more distinct.

C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Bacteria of Normal Milk Fæces. By A. BAGINSKY (*Zeit. physiol. Chem.*, 12, 434—462).—These observations were undertaken in hope that they might throw some light on the disorders of the

alimentary canal of suckling children. Escherich (*Die Darmbakterien des Säuglings*, Stuttgart, 1886) has shown that in the normal fæces of such children there are many forms of micro-organisms, but he dealt especially with two, the *B. lactis ærogenes* and the *B. coli commune*. In the present research these were separated and cultivated by the best modern methods, and portions of the pure cultivation of *B. lactis* (with which this paper exclusively deals, and which is so called on account of its supposed action in forming lactic acid from milk-sugar) were added to portions of the substances used as food by children.

With milk-sugar, an acid reaction is always produced, and after 20 days' fermentation about 80 per cent. of the sugar has disappeared. During the first few days, there is abundant formation of gas (carbonic anhydride, hydrogen, and methane). The merest traces of lactic acid are found, and sometimes it is entirely absent. In the distillate, traces of acetone are present. The acid formed is acetic acid. The same change occurs in the absence of oxygen; addition of bile to the mixture causes no difference. Lactic acid is not an intermediate product, for the action of the bacterium on lactic acid is to transform it not into acetic but into butyric acid.

The chief action of the ferment on starch is also to form acetic acid, but only small quantities are formed in the absence of oxygen. No reducing substance is ever produced. The ferment has no action whatever on casein; the total proteid in milk before and after fermentation is the same. There are no products of the fermentation of proteids (leucine, &c.) to be found; and the acid reaction seems to be simply due to the formation of acetic acid from milk-sugar. The power of various antiseptics to stop the fermentative action of the bacterium are finally adverted to; among the facts mentioned, the most interesting is the power of calomel both to stop the activity of the ferment, and to cure certain forms of infantile diarrhœa. The name *B. aceticum* (instead of *B. lactis*) is suggested.

W. D. H.

Influence of Filters on the Constitution of Water. By A. J. C. SNYDERS (*Ber.*, 21, 1683—1691).—The author's results are given in tabular form, showing the bacteriological and chemical difference between various samples of filtered and unfiltered water after various lengths of time.

Sea-sand removes the greater part of the micro-organisms, but not all; it likewise exercises some slight chemical action on the water.

Chamberland-Pasteur filters (compressed asbestos) remove all bacterial germs for at least two months, but their chemical action is quite inconsiderable. The Chamberland filter (animal charcoal) has, however, a not inconsiderable chemical action, inasmuch as it removes the solid constituents, organic substances, chalk, and magnesia; ammonia, the nitrites, iron, and lead are partially kept back, but the chlorides are not acted on.

Maignen's "watch-filter" (carbo-calcis) removes all bacteria at first, but its action does not continue as long as that of the Chamberland filter. On the other hand, it has a very important chemical purifying action; about two-thirds of the solids are removed, the quantity of

ammonia and nitrites greatly diminished, and the whole of the organic substances, iron, and lead eliminated. The chlorides are not acted on.

F. S. K.

Proteolytic and other Ferments in Oats, and their Action on Digestive Organs. By ELLENBERGER and V. HOFMEISTER (*Bied. Centr.*, 1888, 319—321).—A mixture of oats and water develops three ferments, an amylolytic, a proteolytic, and a lactic, all of which are destroyed at 100°; the action of such ferments greatly aids digestion, whereas increased activity of the digestive organs is required if the food is previously boiled. The principal of the ferments is the amylolytic, 2 per cent. of sugar being produced in three hours, or 2 per cent. lactic acid and 3·2 per cent. sugar in seven hours. The lactic ferment is much feebler, the action in three hours being only 0·5 per cent., and in 6 to 7 hours 1 per cent. Ice-cold water retards the action. The result of giving boiled food generally to Graminivoræ is to produce catarrh of the stomach, &c., because by the destruction of the ferments unusual action of the digestive organs is necessitated.

E. W. P.

Diastase. By J. FANKHAUSER (*Bied. Centr.*, 1888, 205—207).—During the germination of barley, the development of the plumule is accompanied by the destruction and solution of the cell walls in the grain. This solution may be due either to a substance formed by the embryo, namely diastase, or to micro-organisms; a microscopical examination, however, failed to show the presence of the latter.

Experiments showed that during germination both of potatoes and of barley, the evolution of carbonic anhydride is accompanied by the secretion of one or of several powerful acids. Malt treated with 5 per cent. solution of potash yielded an extract, which after suitable treatment gave a distillate, in which formic acid was the chief constituent. It was found that both this distillate and also commercial formic acid had the power of changing a carbohydrate into sugar.

The author believes that the cell walls of the starch granules which are in direct contact with the plumule are attacked by the formic acid it secretes, and that in the course of brewing, the formic acid acts on the starch just as dilute sulphuric acid would. He also attributes the sweetness that potatoes acquire to a similar cause; formic and probably other allied acids are formed during the respiratory process that accompanies sprouting, and these acids attack the cell walls and also change the starch into sugar. Many other phenomena of plant growth can be explained by this secretion of strong acids by organs containing no chlorophyll, for instance, the piercing of wood by the mycelia of fungi.

H. H. R.

Function of the Colouring Matter of Chlorophyll. By A. HANSEN (*Bied. Centr.*, 1888, 357—358).—Like the colouring matter of blood, the absorption-bands of chlorophyll have no connection with the assimilative power of the same. The colouring matter absorbs carbonic anhydride, and forms with it an unstable compound, which passes on the carbonic anhydride to the plasma of the chlorophyll

grains. For the formation of 25 grams of starch about 20 litres of carbonic anhydride (50 cm. air) are requisite, this quantity must pass over a square meter of leaf surface in 15 hours. Chlorophyllous cells absorb more and more gas as the temperature rises, consequently the law of diffusion and absorption of gases is not followed in this case; but the absorption is dependent on atmospheric pressure. E. W. P

Formation of Organic Acids, Nitrogenous Compounds, and Potassium Nitrate in Beetroot. By H. LEPLAY (*Compt. rend.*, 106, 1020—1022).—Sugar-beet was sown in Fontainebleau sand, which had previously been heated to redness to remove organic matter and then mixed with 1 per cent. of calcium phosphate and 1 per cent. of calcium sulphate. The crop was watered daily with a liquid which contained in each litre 0.1 gram of potassium hydrogen carbonate, 0.1 gram of ammonium hydrogen carbonate, 100 c.c. of a saturated solution of calcium sulphate, and 100 c.c. of a saturated solution of carbonic anhydride. The beet was sown on May 26th, and the crop gathered on October 14th. During growth, the plants and soil were freely exposed to the air, but were protected from rain. The quantity of each substance in the crop for every one part of the same substance in the seeds was as follows:—Total matter, moist, 74.7; water, 581.00; dry solid matter, 8.66; organic and nitric nitrogen, 10.32; nitric nitrogen in the leaves, 15.50; potassium combined with organic acids, 17.43; calcium combined with organic acids, 17.38.

No calcium, ammonium, or potassium was present either in the form of oxides, or as hydrogen carbonate, and hence the nitrogen which is absorbed as ammonia becomes converted into nitrogenous organic compounds, and the calcium and potassium absorbed in the form of hydrogen carbonates are transformed into salts of organic acids (compare Abstracts, 1886, 830). C. H. B.

Synthesis of Albumin in Chlorophyll-containing Plants. By CHRAPOWITZKI (*Chem. Centr.*, 1888, 185, from *Bull. Acad. St. Petersb.*, 32, 96—98).—Plants which consume their own reserve supply of albumin when deprived of a supply of nitrogen, were used to determine the position where the new formation occurred. After exposing them to light, in mineral solutions free from nitrogen, until the albumin had disappeared from the leaves, they were transferred to nutrient solutions containing nitrogen.

Three to six days after the transference from the non-nitrogenous to the nitrogenous soil, an accumulation of albumin was found in the chlorophyll grains. The author concludes that the chlorophyll substances not only synthesise carbohydrates, but albumin also.

J. P. L.

Some Nitrogenous Constituents of the Seedlings of Soja Hispida. By E. SCHULZE (*Zeit. physiol. Chem.*, 12, 405—415).—These researches are a continuation of previous observations on the seedlings of *Lupinus* and pumpkins (Abstr., 1887, 369, 747, &c.). The method adopted for the separation of the various bases are variations on those of Brieger. The bases were purified by recrystallisation, their characteristic tests were tried, and finally they, or some

characteristic salts, were subjected to elementary analysis. The final results showed that many bases, the products of retrogressive metabolism, exist; these resemble in kind those of *Lupinus* rather than those obtained from pumpkin sprouts, the chief difference being the almost complete absence of arginine in the seedlings of soja. The etiolated lupin-seedlings yield asparagine in great abundance, amido-valeric acid, phenylamidopropionic acid, arginine, choline, substances of the xanthine-group, and doubtful traces of leucine and tyrosine. The pumpkin sprouts yield very little asparagine, much glutamine, leucine, tyrosine, arginine, choline, vernine, and substances belonging to the xanthine-group. Richardson and Crampton have shown the presence of allantoin in young wheat stalks. The amount of asparagine yielded by the soja seedlings was 7 to 8 per cent. of the dry material.

W. D. H.

Distribution of Amygdalin and Emulsin in Almonds. By W. JOHANNSEN (*Bied. Centr.*, 1888, 326).—Amygdalin is found only in the parenchyma cells of the cotyledons. Emulsin was estimated by determining the fermentative power of the several portions of the almond. It appears that there is present in bitter almonds an amount of emulsin sufficient to convert 40 times the quantity of amygdalin usually present. Besides being present in the root shoots, it is also found in the fibrovascular bundles of the cotyledons, whereas it is only absent from the parenchymatous tissue of the curved sides of the cotyledons. Emulsin is likewise found in a similar situation in sweet almonds. The emulsin does not act on the amygdalin, owing to the fact that they are not in contact, but in different parts of the almond.

E. W. P.

Substance containing Sulphur found in Cruciferous Plants.

By J. SMITH (*Zeit. physiol. Chem.*, 12, 419—433).—With the exception of ethereal hydrogen sulphates, the substances in the animal body which contain sulphur are exclusively proteid or derived from proteid. In plants, on the other hand, numerous sulphur-containing substances are found, the direct relationship of which to proteid is not yet proved. Moreover, these substances are limited to certain natural orders, among which are the Crucifers. Bussy (*Annalen*, 34, 223) has described potassium myronate in black mustard. Will (*Chem. Centr.*, 148) has described a glucoside, sinalbin, in white mustard seeds; other similar observations are quoted.

The amount of uncombined and of combined (as ethereal hydrogen sulphates) sulphuric acid was estimated in the seeds of 19 varieties of Crucifers; the former occurs either not at all, or in mere traces, except in *Isatis tinctoria*, and here it is probably in the shell of the seed. The ethereal hydrogen sulphates were found abundantly in all, but especially in the seeds of *Sinapis nigra*. In this form of mustard seed, about one-third of the total sulphur is combined as proteid, the remaining two-thirds as myronic acid. A ferment in the seeds splits up the glucosides or the ethereal hydrogen sulphates; this occurs at the summer temperature, when the powdered seeds are suspended in water. In some seeds (for instance *Brassica napus*), the process occurs slowly, and at the end of two days has hardly begun; in other cases

(for instance, *Sinapis alba* and *Lepidium sativum*), it is almost completed in the same time. The ferment action can be stopped at any time by the addition of 0.3 per cent. of hydrochloric acid. Simultaneously there is an increase in the amount of uncombined sulphuric acid. This is illustrated by tables of analyses. An exactly similar change occurs in the germination of the seeds. Further it is shown that the seeds of one species freed from ferment by boiling, can be acted on by mixture with the seeds of another species, but there is considerable variation in the activity of the ferments prepared from various species.

W. D. H.

Influence of Manures on the Composition of Barley. By KRANDAUER (*Bied. Centr.*, 1888, 297—298).—"Chevalier," "Franken," and "Halletts" barley were manured with nitre and guano superphosphate, and with nitre with half as much again of superphosphate. Only Franken barley answered to the smaller admixture of superphosphate as regards the grain, but an increase of straw was obtained in all cases. No decided increase of nitrogenous matter was induced.

E. W. P.

Effect of Chemical Manures on the Composition of Soja. By A. LEVALLOIS (*Compt. rend.*, 106, 1014—1017).—The soil employed in these experiments contained per kilo., 0.424 gram nitrogen, 0.480 gram potassium oxide, and 0.639 gram phosphoric anhydride. Two plots were planted with soja, and one of them was treated with a complete chemical manure. The manured plot gave a much heavier crop, but the proportion of grain was smaller, and its quality inferior. In the manured crop, the weight of the grain was to the total weight of the plant as 1 : 3.9, whilst with the unmanured crop, the ratio was 1 : 1.9. Moreover, in the latter case the grains were larger and more regular. The following table gives the proportion of various constituents in 100 grams of the dry grain in each case:—

	N.	P ₂ O ₅ .	K ₂ O.	Oil.	Substances soluble in alcohol.
Manured . . .	6.16	1.25	3.03	19.06	22.20
Unmanured..	6.27	1.47	3.16	20.33	19.60

The differences are probably due to the fact than in the first case the grains are smaller, and hence there is a greater proportion of testa to a given weight of grain.

C. H. B.

Relation between Atmospheric Nitrogen and Vegetable Soils. By T. SCHLOESING (*Compt. rend.*, 106, 982—987, 1123—1129).—The author has repeated his former experiments (this vol., p. 747), but has modified the method of manipulation in order to avoid the presence of mercury vapour, which is injurious to certain lower organisms. The soils employed were those of Grenelle and Montretout, which are comparatively poor in organic matter, and the results agree with those previously obtained; that is to say, that whilst there is a decided absorption of oxygen, the quantity of nitrogen removed from the atmosphere is too small to be measured by eudiometric methods.

The second paper is a reply to Berthelot (next Abstract). The author points out that Boussingault recognised that soils contain living organisms which exert an important influence on the formation and destruction of ammonia and nitrates. The conditions in his own experiments were not materially different from those in which Berthelot and André obtained evidence of the direct absorption of atmospheric nitrogen. The soils employed contained from 7 to 19 per cent. of clay, which is a considerable proportion, and the methods of endiometric analysis are at least as accurate as determinations by means of soda-lime.

C. H. B.

Absorption of Nitrogen by Soils. By BERTHELOT (*Compt. rend.*, 106, 1049—1055).—A criticism of Schloesing's papers (this vol., p. 747 and preceding Abstract). The conditions in Schloesing's experiments were not similar to those in which the author and André proved the direct absorption of atmospheric nitrogen, and the analytical results cannot be accepted as accurate, because of the difficulties of manipulation inseparable from endiometric methods, and also on account of the small quantity of soil employed. It is pointed out that Boussingault regarded the soil simply as a chemical supporter of vegetation, and had no regard to the minute living organisms which are always present.

C. H. B.

Absorption of Nitrogen by Vegetable Soils. By BERTHELOT (*Compt. rend.*, 106, 1214—1215).—A further reply to Schloesing.

Absorption of Nitrogen by Soils and Plants. By A. GAUTIER and R. DROUIN (*Compt. rend.*, 106, 1098—1101, 1174—1176, 1232—1234).—The experiments were made with the artificial soils already described (this vol., p. 746). Determinations of nitric nitrogen always gave negative results, and hence it follows that nitrates are not the only source from which plants can obtain their nitrogen.

In all the experiments with soil free from organic matter, there was a loss of ammoniacal nitrogen, a gain of organic nitrogen, but a loss of total nitrogen. In the case of the soils containing organic matter, there was a gain of total nitrogen, and a gain in organic nitrogen, but a loss of ammoniacal nitrogen.

When the soil is supporting a crop, there is always a gain of total nitrogen and a gain of organic nitrogen, but a loss of ammonia. The gain in organic nitrogen is greatest with the soils which contain organic matter.

The loss of ammoniacal nitrogen in the case of the soils free from organic matter, is due to cryptogamic vegetation. A green coloration is observed on the surface of the soil, and this consists of unicellular algæ, such as *Pleurococcus vulgaris* and *Protococcus viridis*. They probably act, not by directly absorbing nitrogen from the air, but by converting into organic nitrogen the ammoniacal nitrogen.

The general conclusions arrived at from these and previous results (*loc. cit.*) are as follows:—Soil absorbs nitrogen from the air, provided that it contains organic matter, which is an indispensable agent in the process. Iron oxides accelerate the absorption, but are not essential.

Whatever may be the initial form of the nitrogen absorbed, it is converted into organic nitrogen. On the other hand, the soil continually loses the ammoniacal nitrogen brought to it by the wind and rain, or produced by bacterial fermentation in the soil itself. The permeability of the soil, its degree of subdivision and compression, are important factors, and if the soil is rammed down, or is rendered more or less impervious by the presence of excess of clay, very much less nitrogen is absorbed; hence the necessity in practice for a repeated breaking up and renewal of the surface. In the experiments described, the total quantity of nitrogen assimilated in three months in soil without plants is, for the area of surface exposed, 10 times as great as the ammonia absorbed by dilute acid in Schloesing's experiments. Since nitrates were absent it follows that there are in the air other substances besides ammonia and nitric acid from which nitrogen can be assimilated. The growth of plants on the soil results in more than double the increase in the quantity of nitrogen absorbed, and it follows that phanerogamic plants absorb, indirectly through the soil in which their roots are placed, or directly by their leaves, some of the free or combined nitrogen in the atmosphere, and fix it in their tissues.

Unicellular aerobic organisms, and especially certain species of algæ, which are universally distributed over the surface of arable soils, play an important part in the absorption of nitrogen by the soil, even when the latter is free from vegetable organic matter.

C. H. B.

Value of Nitrogen in Sodium Nitrate and in Ammonium Sulphate. By G. KLIEN (*Bied. Centr.*, 1888, 166—168).—Experiments were made on four different estates as to the comparative value of the nitrogen in these manures applied to oats and barley. In the results obtained, nitrogen in the one form appears sometimes better, sometimes of equal value, and sometimes inferior to nitrogen in the other form, so that no general conclusions can be drawn.

H. H. R.

Experiments with Farmyard Manure. By E. HEIDEN (*Bied. Centr.*, 1888, 154—165).—Strewing the manure in the stalls with superphosphate dried by gypsum, to the amount of 2 lbs. daily for every 1000 lbs. of live weight of the cattle, was found to cause a greater weight of manure, and a manure richer in nitrogen and phosphates than when this treatment was omitted. Further the manure thus treated lost less dry matter on keeping, and when used for potatoes gave a better yield than the untreated manure.

In the case of manure allowed to remain beneath the cattle for weeks, the effect of strewing with superphosphate dried by gypsum was found to be the production of a greater weight of manure, of dry manure substance, and also of manurial nitrogen.

Sulphuric acid containing phosphoric acid has recently been introduced in commerce as an agent for preventing the loss of combined nitrogen from liquid manure. The author experimented with a sample containing 3.72 per cent. of phosphoric acid, and 24.49 per cent. of sulphuric acid, adding it to the liquid manure in quantity sufficient to produce a slightly acid reaction, and repeating the addition several

times in order to secure this. He found that it saved a large proportion of the nitrogen that otherwise would have been lost.

H. H. R.

Prevention of the Loss of Nitrogen in Farmyard Manure.
By B. C. DIETZELL (*Bied. Centr.*, 1888, 168—171).—Loss by volatilisation of ammonia and ammonium carbonate can be sufficiently prevented by treading the manure well down and keeping it moist, without employing kainite, gypsum, or ferrous sulphate to retain the ammonia. Loss by the formation of free nitrogen is not prevented by the addition of gypsum, calcium carbonate, or earth, and kainite only checks it by hindering decay, and the action ceases when the manure is applied to the land. The addition of sulphuric acid to liquid manure is not more effectual.

In some manuring experiments the author observed that no loss of nitrogen occurred in a soil manured with superphosphate. He explained the phenomenon by the supposition that calcium phosphate reacts with ammonium nitrite, and so prevents the action of nitrous acid on primary amines and amido-acids, and the consequent evolution of free nitrogen. Further experiments, in which precipitated phosphate and basic slag meal were used, confirmed his previous observation. He recommends that part of the phosphatic manure, instead of being put on the field, should be previously mixed with the farmyard manure, and in the case of liquid manure, that superphosphate should be placed in a basket and suspended in the liquid.

H. H. R.

Analytical Chemistry.

Testing Mercury Oxides for Chlorides. By T. FELS (*Arch. Pharm.* [3], **26**, 29—30).—The silver nitrate test is much more sensitive when the oxide is dissolved in acetic acid than when either nitric or sulphuric acid is used as the solvent. J. T.

Detection of Copper in Wine. By GIGLI (*Arch. Pharm.* [3], **26**, 273—274, from *L'Orosi*, 1887, 397).—200 c.c. of wine is concentrated to one-fifth and strongly acidified with hydrochloric acid, when a small zinc-platinum couple is immersed. Any copper which may be present is deposited on the platinum plate within 24 hours. Iron alone causes no deposition on the platinum, but if copper is present, the two metals are deposited together, and require separation before the copper can be estimated quantitatively. J. T.

New Method for the Estimation of Manganese. By L. SCHNEIDER (*Monatsh.*, **9**, 242—254).—Bismuth tetroxide, in presence of a large quantity of nitric acid, oxidises manganous salts to permanganic acid quickly and completely at the ordinary temperature. When about 2 c.c. of nitric acid, sp. gr. 1.2, is present for every 1 mgm. of manganese, no precipitation of manganese peroxide occurs, and on

adding an excess of finely-divided bismuth tetroxide, oxidation is complete in a few minutes. The presence of considerable quantities of ferric oxide or sulphuric acid does not affect the results. This process can be employed for the estimation of manganese in iron, steel, &c., as follows:—5 grams of steel or iron, poor in manganese, is dissolved in 100 c.c. of nitric acid, sp. gr. 1·2; when solution is complete, the whole is boiled for some time, allowed to cool, and about 100 c.c. of nitric acid, sp. gr. 1·2, added. The mixture is then digested for a few minutes with about 10 grams of bismuth tetroxide. In the case of iron which contains several per cent. of manganese, 1 gram is dissolved in nitric acid, and the solution diluted with 20 to 300 c.c. of the same acid. Ores or dross which are insoluble in nitric acid are boiled with hydrochloric acid, then treated with hydrofluoric acid and evaporated with sulphuric acid. In analyses of spiegeleisen rich in manganese, ferromanganese, and rich manganese ores, the solution containing 1 gram of the substance is diluted to 1 litre with water, 200 c.c. of this solution taken, mixed with 100 c.c. of concentrated nitric acid, and oxidised with bismuth tetroxide as before. When oxidation is complete, the solution of permanganic acid is filtered from the bismuth tetroxide through an asbestos filter, and titrated with a solution of hydrogen peroxide. This method can be carried out in about an hour, and the results are very satisfactory. The presence of free nitric acid is necessary during titration. The hydrogen peroxide employed for titrating the permanganic acid, is standardised by adding dilute nitric acid (1 vol. concentrated acid with 2 vols. of water) to a known quantity of potassium permanganate, until about 2 c.c. of nitric acid, sp. gr. 1·2, is present for every 1 mgm. of manganese, and then adding ordinary commercial hydrogen peroxide, diluted to about 0·5 per cent., until the colour disappears.

Bismuth tetroxide is best prepared by heating equal parts of bismuth oxide and potassium chlorate until the mixture ceases to glow, and then adding 2 parts of soda. The cold melt is washed with water until free from alkali, and the residue, which is a compound of sodium and bismuthic acid, agitated with 5 per cent. nitric acid. The dark, reddish-brown substance, which settles to the bottom is washed with water and dried. The composition of this compound, dried over sulphuric acid, is $\text{Bi}_4\text{O}_8\cdot\text{H}_2\text{O}$. F. S. K.

Estimation of Free Oxygen in Water. By LATIEU (*Arch. Pharm.* [3], 26, 128, from *J. Pharm. Anvers*, 1887, 570).—About 200 c.c. of water is treated with a definite quantity of sodium hydroxide and ferrous-ammonium sulphate solution in a narrow necked flask, closed by a perforated stopper. The precipitate formed is again dissolved by the addition of a definite volume of dilute sulphuric acid, and standard permanganate solution is added, corresponding with the excess of ferrous solution remaining. The excess of ferrous solution added above that indicated by the permanganate solution measures the free oxygen present. J. T.

Estimation of the Hardness of Waters. By E. v. COCHENHAUSEN (*J. pr. Chem.* [2], 37, 413—416).—The author objects to

titrating a soap solution with calcium chloride or barium chloride, inasmuch as these salts are seldom or never found in natural waters, and have been shown to differ in their actions on soap solution from those that are generally contained in waters. The soap solution should be standardised by a solution of calcium sulphate, made either by diluting a solution saturated at a known temperature, and therefore of a known strength, or by titrating a saturated solution of lime water to neutrality with sulphuric acid of known strength, and diluting the calcium sulphate solution thus obtained until it contains an amount of sulphate equivalent to the quantity of calcium chloride generally employed. Before determining the hardness, the carbonates in the water are converted into sulphates by adding a slight excess of centinormal sulphuric acid, and titrating back accurately with centinormal alkali.

A. G. B.

Detection of Impurities in Commercial Alcohols. By L. GODEFROY (*Compt. rend.*, 106, 1018—1020).—6 or 7 c.c. of the alcohol is agitated with one drop of perfectly pure benzene, mixed with 6 or 7 c.c. of pure sulphuric acid of 66°, and again agitated. If reducing "head" products are present, the liquid immediately acquires a coloration which gradually darkens for a few minutes, and varies from pale brownish-yellow to black. Pure ethyl alcohol gives no immediate coloration, but after 8 or 10 minutes the liquid acquires a slight rose tint. This test will detect 1 c.c. of "head" products in 1000 litres of alcohol, or 1 part per 1,000,000. The quantity may be estimated by comparing the colour with that given by alcohol containing a known quantity of acetaldehyde, and expressing the results in terms of the latter.

If the liquid remains colourless after several minutes, no "head" products are present. In order to detect "tail" products, care is taken that the acid and alcohol are thoroughly mixed, in order to avoid polymerisation, and the liquid is boiled for a short time and then allowed to remain for several minutes. Under these conditions, pure ethyl alcohol gives an ochre-yellow coloration; but in presence of "tail" products the liquid acquires a brown colour with a green fluorescence, the depth of tint increasing with the quantity of impurity. This test is not so sensitive as the first, but will detect 1 part in 100,000.

Neither of these tests is directly applicable to wines, spirits, &c. These liquids should be distilled, and the first fraction tested for "head" products, and the last fraction for "tail" products.

C. H. B.

Estimation of Glucose by Fermentation. By GRÉHANT and QUINQUAUD (*Compt. rend.*, 106, 1249—1250).—Estimations of glucose by fermentation are vitiated by the fact that carbonic anhydride is given off by the respiration of the yeast. If comparative experiments are made with equal quantities of yeast, the glucose being omitted in one case, the correction required can readily be determined, and the method then becomes accurate, and is especially suitable for dilute solutions which contain organic matter. Fermentation proceeds

equally well under atmospheric pressure or in a vacuum, but in the latter case the carbonic anhydride produced by the respiration of the yeast is, of course, much smaller.

C. H. B.

Estimation of Reducing Sugar. By R. GEDULT (*Chem. Centr.*, 1888, 201, from *Mon. Sci.* [4], 2, 62—63).—This process, which dispenses with the filtration and reduction of cuprous oxide, depends on the decomposition of cuprous oxide by ammoniacal silver chloride according to the formula $2\text{AgCl} + \text{Cu}_2\text{O} = 2\text{Ag} + \text{CuO} + \text{CuCl}_2$, and the subsequent titration of the chlorine as CuCl_2 with silver nitrate after acidifying the solution. The preparation of standard solutions and the general mode of procedure is given in detail in the original.

J. P. L.

Testing Beet-sugar for Purity. By A. IHL (*Bied. Centr.*, 1888, 287).—Pure sugar dissolved in sodium hydroxide solution does not decolorise methylene-blue when boiled, whereas the smallest amount of invert sugar, grape-sugar, or dextrin, &c., decolorises methylene-blue.

E. W. P.

Adulteration of Olive Oil. By R. BRULLÉ (*Compt. rend.*, 106, 1017—1018).—10 c.c. of the oil is mixed with 0.1 gram of dried powdered egg albumin and 2 c.c. of ordinary nitric acid, and the mixture is uniformly and gently heated. When the acid boils, the tube is inclined so that the albumin mixes with the oil, and if the latter is pure it acquires a greenish-yellow colour; but if mixed with not less than 5 per cent. of seed oils, it has an amber-yellow colour, and if the quantity of foreign oils approaches 50 per cent., the colour is deep orange. Nitric acid alone gives similar colorations, but only in presence of oils which are themselves coloured. The author has used this test with satisfactory results with earth-nut, sesame, poppy, colza, camelina, and linseed oils. Commercial so-called exotic aveline oil gives a rose tint with white streaks.

C. H. B.

Estimation of Nicotine in Tobacco Extract. By J. BIEL (*Arch. Pharm.* [3], 26, 322, from *Pharm. Zeit. Russ.*, 27, 3).—The extract, diluted with water, is treated with sodium hydroxide and distilled in a current of steam until the distillate no longer has an alkaline reaction. The distillate is faintly acidified with sulphuric acid, concentrated to one-tenth its volume, made alkaline with sodium hydroxide, and agitated with ether six times. The ethereal extract is evaporated to remove the ether and a little ammonia which may be present, the residue taken up with decinormal sulphuric acid, and the excess of acid titrated back with decinormal soda solution, using rosolic acid solution as indicator. About 7 per cent. of nicotine corresponds with a good extract.

J. T.

Estimation of Caffeine in Guarana. By A. KREMEL (*Arch. Pharm.* [3], 26, 318, from *Pharm. Post*, 21, 101).—10 grams of guarana powder with 100 c.c. of 25 per cent. alcohol are placed in a

flask and the total weight noted. After digesting for one to two hours on the water-bath and cooling, the weight lost is made up with similar alcohol, and 50 c.c. (= 5 grams guarana) is filtered off, mixed with calcium hydroxide, and evaporated to dryness. The finely powdered residue is extracted with chloroform, from which extract the caffeine is obtained in beautiful crystals on evaporation: these are dried at 100° and weighed. Commercial samples gave 3.12 to 3.8 per cent. of pure caffeine. The ash of guarana amounts to 1.3 to 2.0 per cent., and is rich in phosphates.

J. T.

Detection and Estimation of Magenta in Orchil and Cudbear. By C. RAWSON (*Chem. News*, 57, 165).—The following method is recommended as an improvement on the methods hitherto suggested for the detection and estimation of magenta in orchil and cudbear. 1 or 2 grams of cudbear, or an equivalent of orchil liquor, is boiled with 50 c.c. of alcohol, then diluted with 100 c.c. of water, and mixed with 15 to 20 c.c. of a strong solution of basic lead acetate, and a similar quantity of strong ammonia. The cudbear or orchil colouring matter is completely precipitated. On acidifying the filtered solution with acetic acid, the presence of magenta becomes apparent, and may be verified by testing; in this way 1 part of magenta may be detected in 100,000 parts of cudbear. The magenta is estimated colorimetrically by comparison with a standard solution of p. 12 magenta.

D. A. L.

Two Methods for Detecting Vinoline. By E. POLLACCI (*Chem. Centr.*, 1888, 86, from *Ann. Chim. Farm.*, 87, 308—311).—The first method consists in mixing 6 to 7 c.c. of wine with nickel oxide to a thin paste, and allowing it to remain two to three hours. After this time, pure wine would be decolorised. The mixture is filtered, the residue washed with water, and then treated with 3 to 4 c.c. of a mixture of equal volumes of water, methyl and ethyl alcohols, strongly acidified with sulphuric acid. If the filtrate is red, vinoline is present.

The second process depends on the decomposition of the natural colouring matter of wine by lead peroxide, and the conversion of vinoline into a very yellow oxidation-product, which acids turn red, ammonia blue. The yellow colour changes to a beautiful violet after simple exposure to air. To test wine, 5 to 6 c.c. is mixed with lead peroxide, well stirred for two minutes and filtered. If the filtrate after the addition of hydrochloric acid remains colourless, vinoline is absent.

J. P. L.

Detection of Picrotoxin in Beer, &c. By R. PALM (*J. Pharm.* [5], 17, 19—20, from *Pharm. Zeit. Russ.*).—A solution of picrotoxin in either water or alcohol, when agitated with freshly-prepared lead hydroxide until the liquid has lost its bitterness, gives a stable compound between the alkaloïd and the lead. The least trace can be thus isolated, and the compound moistened with concentrated sulphuric acid gives a beautiful, saffron-yellow coloration, as well as if the alkaloïd were isolated in the pure state. It is essential that the

hydroxide should be freshly-prepared and well washed to free it from ammonia or potash. Lead carbonate, bismuth hydroxide, and other metallic hydroxides do not precipitate the alkaloid. The suspected liquid is evaporated to dryness, the residue is taken up in very little water, slightly acidified, filtered, and shaken with ether. The residue from the ether is dissolved in a little water, filtered through animal charcoal, and the liquid completely precipitated by lead acetate, avoiding excess of this reagent. The filtered solution is finally well shaken with freshly-prepared lead hydroxide, and the yellow colour is obtained with sulphuric acid if picrotoxin is present. The colour persists several hours, and disappears on addition of an alkali, to reappear on addition of strong acid. J. T.

Estimation of Urethane in Urine. By G. JACQUEMIN (*J. Pharm.* [5], 16, 538—539, from *J. pharm. Alsace-Lorraine*).—500 c.c. of urine is well shaken with ether, which is then separated and well washed to remove all trace of urine. The residue left by the ether on evaporation is dissolved in 10 to 20 c.c. of water, treated with potash in excess, and a standard solution of mercuric chloride is added until a persistent, yellow precipitate is produced. Urethane gives a more or less copious, white precipitate, but if in small amount, a yellow precipitate is formed which redissolves, and the amount of standard solution added when the yellow precipitate becomes persistent is proportional to the urethane present. J. T.

Estimation of Globulin. By POHL (*J. Pharm.* [5], 16, 536, from *Arch. f. ex. Path.*).—The author gives the preference to ammonium sulphate which he adds directly to serous liquids, and to acid urines after preliminary neutralisation with ammonia and separation of the phosphates by filtration. A saturated solution of ammonium sulphate is added to a urine thus neutralised, and after remaining an hour, the precipitate is collected on a tared filter, washed with ammonium sulphate solution, dried at 100°, and weighed. After ignition, the weight of the ash is deducted. J. T.

The Furfuraldehyde Colour Reaction. L. v. UDRÁNSZKY (*Zeit. physiol. Chem.*, 12, 355—376; compare this vol., p. 863).—Mylius (*Abstr.*, 1887, 1149) has shown that the red colour produced by heating the bile acids, sugar, and sulphuric acid together, is due to the formation of furfuraldehyde from the two last-named reagents. He also showed that although of the substances he examined, the bile acids gave the test in the most marked manner, yet that there exist numerous organic substances that also give a similar reaction.

The present research is chiefly an expansion of Mylius' work. A very large number of organic substances were examined in the following way. A minute particle of the substance under investigation, or a drop of the substance if liquid, was placed in a test-tube with 1 c.c. of water or alcohol, and then a drop of solution of furfuraldehyde; concentrated sulphuric acid was added carefully, and the result watched. The temperature of the mixture was not allowed

to rise over 50° . As solutions of furfuraldehyde of a strength greater than 2·2 per cent. themselves give a coloration with sulphuric acid (showing an absorption-band spectroscopically at D), a solution of the strength 0·5 per cent. was used in all cases, which is a strength considerably greater than Mylius found necessary in the case of the bile acids. Some of the substances examined gave a coloration with sulphuric acid alone; the tint given with furfuraldehyde also varied a great deal; the particulars in each case are stated in a lengthy table. The reaction was found not to be a class reaction. The substances which give a colour are as follows:—Acetal, acetaldehyde, ethyl acetoacetate, acetone, ethylene glycol, malic acid, alizarin, amyl nitrite, anilidoacetic acid, aniline, anisaldehyde, anthracene, anthraquinone, apomorphine, atropine, benzaldehyde, borneol, catechol, brucine, quinic acid, cholesterin, cinchonine, codeïne, coniferin, conine, cumarin, cyanuric acid, cymene, digitaline, dimethylaniline, dihydroxytartaric acid, diphenylamine, gallic acid, Japan camphor, cresol, lævulinic acid, mesitylene, mesityl oxide, metaldehyde, methyl alcohol, methylhydantoin, methylaniline, morphine, naphthalene, α -naphthol, α -naphthascatole, cœnanthaldehyde, orcinol, paraldehyde, paraffin, phenanthrene, phenanthraquinone, phenol, phenylhydrazine, phloroglucinol, phorone, propaldehyde, protocatechuic acid, pyrogallol, resorcinol, salicaldehyde, salicylic acid, scatole, stearic acid, strychnine, toluene, thymol, tyrosine, valeraldehyde, vanillin, vanillic acid, vaselin, veratrine, metaxylene, paraxylene, cinnamaldehyde.

The substances which gave no colour are as follows:—Acetamide, acetanilide, acetophenone, alloxan, alloxantin, aspartic acid, benzonitrile, benzoic acid, succinic acid, hydrocyanic acid, pyruvic acid, butyric acid, caffeine, caproic acid, quinine, chinoline, quinone, quinoxaline, chloral hydrate, chloroform, citric acid, crotonic acid, cyanamide, dextrin, metadinitrophenol, dinitrotoluidine, dulcitol, acetic anhydride, formamide, fumaric acid, fermentation lactic acid, glycerol, glycocine, glycollic acid, glyoxal hydrogen sulphite, uric acid, urea, hippuric acid, isatin, leucine, malic acid, maltose, mandelic acid, mannitol, methylamine, orthonaphthoxyindole, metanitriline, ortho-nitrobenzaldehyde, orthonitrobenzoic acid, orthonitrophenol, orthonitrophenylpropionic acid, oxalic acid, ethyl oxalate, parabanic acid, metaphenylenediamine, phenylacetic acid, picrotoxin, picric acid, piperidine, pyridine, quinol, mucic acid, starch, tannin, tetroxyethylbenzidine, grape-sugar, tartaric acid, trimethylamine, urethane, xyli-dine, cinnamic acid.

The spectroscopic appearances of the colours obtained differ in many cases; in all probability the products are therefore different; particulars in the case of a few of the more important substances are given; in the case of bile there is a band between D and E, and another at F. Several of the substances examined, for instance α -naphthol, give the test with greater delicacy than is the case with cholic acid.

The fact that the test is given by coniferin gave rise to a number of experiments on the colour reactions produced by strips of the wood of the pine and other trees.

In conclusion, the delicacy of the reaction as applied to the

detection of bile is discussed; using a 1 per cent. solution of furfur-aldehyde in the manner already detailed, it is found possible to obtain a colour with 0.000033 gram of cholic acid; a quantity of 0.00005 gram gives a colour sufficiently intense to show its spectroscopic bands; in order to obtain evidence of the presence of bile acids in urine, it is generally necessary first to isolate them from that secretion. Normal urine does not contain bile acids.

W. D. H.

Detection and Estimation of Indican and its Homologues in Urine. By W. MICHAÏLOFF (*J. Russ. Chem. Soc.*, 1887, 326—328).—Of all the methods for the detection and approximate determination of indican in urine in the form of indigotin, that of Senator, as modified by Salkowski, answers the best, but if the urine is too dark, it must be decolorised by the careful addition of basic lead acetate in order to remove urobilin; another disadvantage of this method is the great care which must be taken in the addition of calcium hypochlorite solution or of bromine-water. The author recommends the following method for the complete elimination of urobilin and its chromogen:—The acidified urine is saturated with finely powdered ammonium sulphate and repeatedly extracted with ethyl acetate. The aqueous liquid is then mixed with an equal volume of fuming hydrochloric acid, chloroform is added, and the oxidation performed with a very weak aqueous solution of bromine. In this way an extract is obtained containing indigotin compounds only and free from urobilin. No superoxidation can take place as in the case of the method recommended by Senator and Salkowski, and by the simultaneous oxidation and extraction with chloroform, the indigotin compounds are almost completely extracted.

B. B.

Detection of Blood in Urine. By C. H. WOLFF (*Arch. Pharm.* [3], **26**, 125—126, from *Pharm. Centr.*, **28**, 637).—30 to 60 c.c. of urine is warmed on a water-bath with one-tenth its volume of a 3 per cent. zinc acetate solution. After 10 to 15 minutes, when most of the clear liquid can be poured off, the precipitate is washed on a small filter and dissolved over a test-tube with a little ammonia, followed by water, so that the total amount of liquid does not exceed 4 to 5 c.c. On this is placed a little benzene to exclude air, and two drops are added of a solution of tartaric acid and ferrous sulphate (1 gram each to 10 grams water). The reduced hæmatin can then be detected by means of a pocket spectroscope.

J. T.

General and Physical Chemistry.

Refraction of Light by Ice, and by Water cooled below Zero. By C. PULFRICH (*Ann. Phys. Chem.* [2], **34**, 327—340).—The fact that whilst water attains its maximum density at a temperature of 4° its index of refraction decreases continuously from 0° to 100° is of considerable theoretical importance, as it shows that neither of the expressions $(\mu - 1)/D$ nor $(\mu^2 - 1)/D$ can be more than approximately constant.

The observations of Rühlmann (*Ann. Phys. Chem.*, **133**, 184) and of Damien (*Ann. l'école norm. sup.* [2], **10**, 275) have shown that the index of refraction diminishes again when water is cooled below 0°. The author finds that the index of refraction attains its maximum value at a temperature of about -1.5° . The author confirms Rühlmann's result that the curve representing the relation between the index of refraction and the temperature is not symmetrical on opposite sides of the maximum, resembling in this respect the similar curve for the density.

The author also describes some experiments on the double refraction of ice, and has made some measurements, using the method of total reflection, of the two principal indices of refraction for different rays of the spectrum. He finds that a sheet of ice 3 or 4 mm. thick cut parallel to the surface of solidification behaves like a slice of quartz $\frac{1}{2}$ mm. thick cut perpendicular to the axis.

G. W. T.

Influence of Concentration on Fluorescence. By B. WALTER (*Ann. Phys. Chem.* [2], **34**, 316—326).—It is well known that the intensity of the fluorescent light emitted by a fluorescent solution increases up to a certain point as the dilution is increased, and then diminishes again. The author points out that in order for fluorescence to take place a certain quantity of light, A, must be absorbed, and of this a certain proportion, Fl, is reproduced by the phenomenon of fluorescence. When the solution is diluted, then if A remained constant Fl would be diminished, but A is also diminished by dilution. The author calls the ratio Fl/A the fluorescing power of the solution, and he has made a series of observations on solutions of different degrees of concentration of fluorescein, eosin, and Magdala red, from which he finds that this fraction increases without limit with the dilution of the solution. He considers it probable that the same law holds for all fluorescent substances, as it gives a satisfactory explanation of the apparently anomalous phenomenon referred to, and also of the fact that many substances which are strongly fluorescent in solution show no traces of fluorescence in the solid state.

In the case of a solid or of a highly concentrated solution the ratio Fl/A would be indefinitely small, so that no fluorescent effects would be observed, and, on the other hand, when the dilution increases beyond

a certain amount, although the proportion of light reproduced by fluorescence, to the amount absorbed, will continue to increase, the total amount absorbed will be so small that the fluorescence will be imperceptible. This explanation receives strong support from the fact that fluorescence can be observed in dilute solutions when the total absorption is too small to be measured.

The author considers that the fluorescence exhibited by some solid substances may be explained in the greater number of cases as being due to the dilution of the fluorescent substance by water of crystallisation or other transparent substance.

G. W. T.

Fluorescence of Cupriforous Calcium Oxide. By L. DE BOISBAUDRAN (*Compt. rend.*, 106, 1386—1387).—Calcium oxide which contains a small proportion of cupric oxide and has been calcined in presence of air, shows a very brilliant pale-green fluorescence in a vacuum, but no definite spectrum is observed. If the oxide is heated in hydrogen, the green fluorescence is replaced by a less intense rose or reddish fluorescence. With 0.1 per cent. of cupric oxide, the fluorescence is much more brilliant than with 1 per cent. When the former proportion is present, and the oxide is heated in hydrogen, the calcium-manganese band is seen in the spectrum of the fluorescence. With only 0.002 per cent. of cupric oxide, the fluorescence is more brilliant than with 0.1 per cent., but is white. Both green and red fluorescences diminish if the oxide is heated. The presence of manganese partially prevents the fluorescence due to copper.

C. H. B.

Spectral Analysis of Magnesium and Carbon. By A. GRÜNWARD (*Phil. Mag.* [5], 25, 343—350).—The author uses the method of spectral analysis devised by him for oxygen and hydrogen (*Abstr.*, 1887, 1070). The wave-lengths of the magnesium lines are divided into four groups. The first group, ascribed to the element "b" or helium, when multiplied by the proper factors, gives 21 lines, 15 of which agree with those of the water-spectrum of Liveing and Dewar; the rest divided by 2 give lines of the compound hydrogen-spectrum, and have probably not been observed in the water-spectrum owing to their feebleness. The second group of lines is that due to the element "c" in the same state as it occurs in oxygen. When multiplied by $\frac{3}{2}$ and $\frac{5}{2}$ these lines give lines of the water-spectrum, or lines whose wave-lengths are half those of lines of the compound hydrogen-spectrum. Only three lines due to "c" in oxygen are identical with those of the second group, the extinction of the rest being due to the influence of the other components of magnesium. The third group of magnesium lines is due to the element "b" in the state in which it occurs in hydrogen under the influence of "a" (Coronium). Multiplied by the proper factors these lines give 90 lines, which agree very closely with those of the water-spectrum. The fourth group consists of 50 lines, due to "b," as it occurs in hydrogen in water-vapour, nearly all of which correspond with lines observed by Liveing and Dewar. Only a few of the lines calculated for oxygen are found in the oxygen-spectrum, this being due, the author considers, to their feebleness.

Magnesium then is a compound containing (1) helium without condensation or dilatation, which in magnesium emits only the rays of Group I, all its other rays, including D_3 , being weakened by the other components. (2.) The element "c," in the state in which it occurs in oxygen and carbon. (3.) The element "b," as it occurs in free hydrogen. (4.) The element "b," in the condensed state in which it occurs in the hydrogen of water-vapour.

Carbon examined in the same way is resolved into:—The element "c" as it occurs in oxygen and magnesium, and "b" in four different states: (1) in which its condensation is three-fifths of that which it has in hydrogen; (2) in the same state as it exists in hydrogen; (3) in which its condensation is five-fourths of that which it has in hydrogen; (4) in which its condensation is twenty-five-sixteenths of that which it has in hydrogen.

H. K. T.

Electrochemical Actinometer. By GOUY and H. RIGOLLET (*Compt. rend.*, 106, 1470—1471).—It is known that if copper with a superficial layer of oxide or basic salt is placed in a solution of copper sulphate, its electromotive force varies under the influence of light, but the phenomena are only distinct when the intensity of the light is high. The authors find that if copper coated with a layer of the oxide is immersed in a solution of a metallic chloride, bromide, or iodide, it is very sensitive even to rays of low intensity, and may consequently be used as an actinometer.

A carefully cleaned plate of copper is heated over a bunsen burner until the iridescence is replaced by a uniform tint. The superficial layer then consists mainly of cuprous oxide; if the heating is continued, cupric oxide is formed, and the plate is less sensitive. It may be protected by a layer of melted paraffin whilst cooling.

When a plate thus prepared is placed in a solution of sodium chloride together with a clean plate of copper, the electromotive force of the element is a few hundredths of a volt, the oxidised plate being positive. When exposed to light, the electromotive force increases, the oxidised plate becoming more strongly positive. Instead of plates of different kinds, two oxidised plates may be used, only one being exposed to light. The effect is instantaneous, and disappears when the light is cut off. Diffused daylight produces an alteration of several hundredths of a volt, and direct sunlight an alteration of at least a tenth of a volt. Gas and lamp flames also have a marked effect, and it would seem that the couple is sensitive to all the visible rays. The variation in the electromotive force is greater when the circuit includes a resistance of several hundred ohms. With a Thomson galvanometer, it is possible to recognise the effect of a candle flame at a distance of several metres.

Solutions of bromides behave in much the same way as chlorides, but in solutions of iodides, the couple is less sensitive.

C. H. B.

Electromotive Force produced by the Action of Light on Selenium. By W. V. ULJANIN (*Ann. Phys. Chem.* [2], 34, 241—273).—The fact that an E.M.F. can be produced by the action of light on selenium was discovered by Adams and Day (*Proc. Roy. Soc.*, 25,

113) who found that when one end of a plate of selenium, into opposite ends of which platinum wires had been melted, was submitted to the action of light, a current was produced, in general from the dark to the light electrode, but not infrequently in the opposite direction.

The subject was next investigated by Kalischer (*Rep. Physik.*, **17**, 563), who used an intermittent beam of light, and succeeded in obtaining sounds in a telephone in circuit with the selenium. Fritts (*Amer. J. Sci.*, **126**, 465) used a sheet of gold leaf as one of the electrodes, and illuminated the selenium through the transparent leaf. He succeeded in a good many cases in obtaining a measurable difference of potential between the ends of the selenium plate, and he found that the current arose immediately on exposing one of the electrodes to the action of light, and ceased instantaneously when the illumination ceased, but as long as the illumination was maintained constant, the current remained constant. He came to the conclusion that the current was due to the direct transformation of luminous into electrical energy. He also concluded from his experiments that there was no relation between the sensitiveness of different specimens to the effect of light, in altering the resistance and producing an E.M.F. respectively. His most sensitive specimens (with regard to the production of E.M.F.) were those in which polarisation was most marked.

Siemens (*Phil. Mag.* [5], **19**, 315) made some experiments with some of Fritts's specimens which had been forwarded to him, and confirmed his result with regard to the constancy of the current, and he also expressed his agreement with the conclusion that the current was due to the transformation of luminous into electrical energy.

The present investigation was undertaken at the suggestion of Kundt, principally with a view of finding a trustworthy method of preparing the specimens of selenium.

The specimens of selenium employed were tested by Rose, and were all found to contain traces of sulphur, whilst some of them also contained traces of mercury, antimony, arsenic, lead, bismuth, and copper. The author found a gold leaf electrode unsatisfactory, as it was very liable to peel off, and he ultimately used platinsed glass plates for both electrodes, connection being made with the circuit by means of strips of brass soldered to the platinum surfaces. These thin layers of platinum possessed the great advantage of allowing all the rays of the spectrum to pass with equal freedom. The plates were kept apart and parallel by means of strips of mica, and the selenium was melted in between them and cooled under pressure. In order to reduce the selenium from the amorphous to the crystalline form (in which only an E.M.F. is produced by the action of light) the plates were heated up to 195° in a paraffin bath and very slowly cooled. It was found that the repetition of this process increased the sensitiveness.

When it was desired to exclude the heat rays, the beam of light was made to pass through a solution of alum. When the plates were prepared in this manner, the difference in their behaviour was comparatively small, and no appreciable effect was produced even when 5 per cent. of sulphur was added to the selenium. The experimental results obtained were as follows:—

(1.) The effect of exposing one of the electrodes to the action of light was to produce an E.M.F. acting from the dark to the illuminated electrode. The E.M.F. disappeared completely when the source of light was shut off. The highest E.M.F. obtained was 0.12 volt.

(2.) In the case of plates prepared by other methods, some always gave an E.M.F. in the same direction whichever electrode was illuminated, but in these specimens its value was always greater when the negative electrode was the one exposed to the light.

(3.) When the electrodes were joined up through a metallic conductor the current flowed for hours from the dark to the illuminated electrode without undergoing any variation in strength.

(4.) When both poles were illuminated simultaneously, the E.M.F. could be weakened to any desired extent or reduced to zero.

(5.) The action of the light was found to take place instantaneously, and the current disappeared immediately and completely when both electrodes were darkened.

(6.) Many of the plates prepared were found to be subject to polarisation, but this was found to have no effect on the sensitiveness of the plates to the effect of light in producing E.M.F.

(7.) If the E.M.F. due to polarisation had attained a sufficient value, then the exposure of either electrode to a source of light diminished the E.M.F. With smaller values of the E.M.F., the effect of exposure to light was of the normal character described under (1). The limiting value of the E.M.F. of polarisation, below which the effects of exposure to light are of the normal character, varied greatly for different specimens.

(8.) The resistance of the plates and also their sensitiveness to the production of E.M.F. on exposure to light, in general diminished gradually with lapse of time. The initial resistances in the dark of the specimens employed, varied from 40,000 ohms to 900,000 ohms, and that of the last-named specimen gradually increased up to 1.4 megohm. In the case of plates prepared by the author's method, the effect of exposure to light on the resistance was to diminish it to about one-ninth of its value in the dark, a much greater sensitiveness than was exhibited by any of the plates prepared by other methods.

(9.) The resistance and also the sensitiveness to the production of E.M.F. were found to be considerably increased by passing alternate currents from a small induction coil through the plates, and plates which had lost their sensitiveness through lapse of time were restored to their former condition by the passage of alternate currents for a sufficient length of time. It was also found that in many cases, plates which previously behaved abnormally, could be reduced to the normal condition by the same method.

(10.) When the illumination was feeble, and the heat rays were excluded as completely as possible, the current was found to be proportional to the intensity of the light falling on the electrode, but when the illumination was stronger, and the heat rays were not excluded, the strength of the current increased more slowly than the illumination. In the latter case it would appear that the E.M.F. increases more slowly than the conductivity.

(11.) When light from different portions of the spectrum was employed, the orange-yellow rays were found to produce the greatest effect in the case of a diffraction spectrum, and the greenish-yellow rays in the case of a prismatic spectrum.

The theory adopted by the author for the explanation of his results is as follows :—

He supposes, in the first place, that the selenium exists in the plates in several allotropic forms, some only of which are sensitive to the action of light. He further supposes that the plates contain particles capable of electrolysis, consisting either of combinations of different allotropic forms of selenium or of selenides of the metals present as impurities. He then assumes that the effect of exposure to light is in the first place to transform the sensitive particles into others which are electropositive to them, and in the second place, to facilitate the reunion of the electrolytic particles which have been broken up by the passage of the current. He then discusses the different experimental results, and shows that they may be explained on these assumptions.

G. W. T.

Study of Contact Electricity. By W. OSTWALD (*Zeit. physikal. Chem.*, **1**, 583—610).—These investigations, undertaken with the view of ascertaining the potential differences between different metals and solutions, were carried out by means of dropping electrodes of mercury. Great difficulty was experienced in eliminating the potential difference between the electrodes themselves and the solution, and this could never be entirely accomplished, although it may be reduced to a minimum by proper adjustment of the aperture and regulation of the flow of mercury by its own pressure. The potential differences measured and tabulated are those between zinc, cadmium, tin, lead, iron, copper, bismuth, antimony, silver, and mercury, and solutions of hydrochloric, hydrobromic, hydriodic, nitric, sulphuric, phosphoric, formic, acetic, propionic, oxalic, and benzoic acids. The solutions used were normal, decinormal, and centinormal.

The potential difference between acid and metal depends of course in the first instance on the nature of the metal. For all the solutions examined, zinc and cadmium gave negative, copper, antimony, bismuth, silver, and mercury positive values, whilst tin, lead, and iron gave both positive and negative values, of 0.1 to 0.2 volt. The mean potential was for zinc -0.7 volt, cadmium -0.3 , tin, iron and lead ± 0 , copper $+0.3$ to 0.4 , bismuth $+0.4$, antimony $+0.3$, silver $+0.5$, and mercury $+0.8$. The nature of the acid has a very marked influence, the potential differences being generally smaller for the haloid acids than for the others. The influence of dilution appears generally to be in favour of increasing the negative potential and decreasing the positive one. At the same time the values obtained for the different acids approximate more closely to one another with increasing dilution.

A comparison of the potential differences between the above metals and acids with the heat developed in the reactions between them, shows that the order of these two values is to a great extent similar. If, however, from the heat developed the potential differences be calculated on the assumption that chemical is wholly converted into

electrical energy, the result is altogether unsatisfactory, and one that goes so far to prove that the above assumption of the total conversion of chemical into electrical energy cannot hold good. H. C.

Electrolysis. By W. W. H. GEE and H. HOLDEN (*Phil. Mag.* [5], 25, 276—283).—When a current passing between palladium electrodes is reversed, no gas is evolved at the pole which is now the anode, but streaks are seen descending through the liquid. After some time, the streaks disappear and gas begins to be evolved. Streaks are obtained if, before reversal, the electrodes are removed and cleaned, but not if they are heated to redness. They are not obtained if platinum electrodes are used. With phosphoric acid solutions, similar results are obtained. With sodium hydroxide solutions, descending streaks are obtained from the cathode without reversal, so long as the gas (hydrogen) is absorbed; when it begins to be evolved, the streaks are carried upwards. The authors consider the streaks to be due to the concentration of the electrolyte by electrolysis at one of the electrodes, the movement of the denser fluid being undisturbed so long as the palladium absorbs the evolved gas. If the electrodes are placed horizontally, ascending streaks can be easily observed at that electrode at which the electrolyte is being weakened, the lighter liquid no longer clinging to the metal. The dense streams were tested for palladium salts and hydrogen dioxide with negative results. A titration showed a higher percentage of sulphuric acid than there existed in the original electrolyte.

H. K. T.

Electrolytic Conductivity of Halogen Compounds. By W. HAMPE (*Chem. Zeit.*, 11, 1549—1550; 12, 23—24, 106, 122, 140, 171, 173; compare this vol., p. 211).—Fused bismuth trichloride (m. p. 217°) is a very good conductor. The primary products of the decomposition are bismuth and chlorine, but the former acts at once on the trichloride to form the dichloride, hence the fused mass around the negative pole changes colour as soon as the circuit is closed, and in a short time the whole contents of the tube become brownish-black. When this is the case a portion of the chlorine liberated at the positive electrode combines with the dichloride to re-form the trichloride. On cooling, conductivity ceases with the solidification of the mass, and when the contents of the tube are treated with concentrated hydrochloric acid, an insoluble residue remains, consisting of very finely divided bismuth, produced by the decomposition of the dichloride; in most cases there are also some very small globules of the metal which has escaped conversion into dichloride.

Bismuth dichloride, prepared by fusing together the exact proportions of the trichloride and metallic bismuth, forms an opaque, black mass, which in very thin slices is transparent and dark-brown. It melts at 176° (uncorr.), and gives off vapour of the trichloride at 330°. It is decomposed by concentrated hydrochloric acid into metallic bismuth and the trichloride. In the fused state, it conducts as well as the trichloride, yielding the same primary products; the decomposition is much complicated by secondary reactions, with feeble currents the

liberated chlorine combines with the dichloride to form trichloride, with which the bismuth separated as a fine powder at the negative pole, re-forms dichloride. With stronger currents, a small quantity of chlorine escapes, whilst a corresponding quantity of bismuth is deposited, and provided the temperature has been sufficiently high (280°) is found as small globules.

Bismuth tribromide is a sulphur-yellow substance fusing at 217° to a red-brown liquid, and boiling at about 500° ; the dibromide, prepared in the same way as the corresponding chloride, is a blackish-grey, crystalline substance melting at 202° (uncorr.) to a black liquid. These bromides behave chemically and electrolytically like the chlorides. As platinum is readily attacked, carbon electrodes were used in these experiments.

Molybdenum oxychloride (MoO_2Cl_2) is infusible at ordinary pressures. It forms a yellow solution with absolute ether, which does not conduct, but after agitating with a few drops of water, the current passes, and the negative pole becomes coated with molybdic molybdate. The sub-etheral layer of water conducts readily on account of the hydrochloric acid present; under the influence of the current it becomes intensely blue, and very soon thickens to a magma. The oxychloride is very soluble in absolute alcohol, forming an acid solution, which conducts with evolution of hydrogen and formation of blue molybdic molybdate. The aqueous solution behaves like a hydrochloric acid solution of molybdic acid. Chlorine is evolved at the positive pole, whilst the reducing action of the liberated hydrogen is observed at the negative pole, so that the solution becomes first green, then blue, and some molybdenum molybdate separates, which, however, dissolves if much water is present. By the continued action of the current, molybdenum trichloride is formed, the solution becomes brownish-black and opaque in thick layers, and gives a black precipitate with potash. Green molybdenum oxychloride (MoOCl_4) does not conduct either in the fused state or in solution in ether, in which it dissolves to a red solution, becoming pale-yellow. Exposed to air it becomes covered with a red film, attracts moisture, and gives off hydrogen chloride. When quite pure it dissolves in water with a yellow colour, and the solution behaves towards the electric current like a hydrochloric acid solution of molybdic acid, but if the oxychloride (MoOCl_4) contains even the smallest quantity of tetrachloride, molybdenum molybdate forms, and the aqueous solution becomes blue in consequence. The violet oxychloride ($\text{Mo}_2\text{O}_3\text{Cl}_6$) dissolved in ether does not conduct, but in aqueous solution decomposes and behaves, with the current, like the other molybdenum oxychlorides.

Tungsten hexachloride, prepared by burning the metal in dry chlorine free from air, and purified by repeated sublimation, is a violet crystalline mass, which decrepitates on heating, melts at 275° , and boils at 346.7° . Tungsten pentachloride is readily crystalline, black in colour, but with green streak; m. p. 248° ; b. p. 275.6° . Its vapour is greenish-yellow. Water decomposes it, with the formation of the bluish-black oxide. Tungstic tetra- and tri-chlorides are not fusible. The oxychloride, WOCl_4 , forms red, transparent needles, melts at 210° ,

and boils at 227.5° . The oxychloride, WO_2Cl_2 , decomposes on heating. None of these tungsten compounds conduct.

Uranium tetrachloride is only obtained free from oxychloride by igniting an intimate mixture of uranous oxide and charcoal in a stream of dry chlorine, and allowing the products to pass over a long length of ignited charcoal before condensing in the drawn-out parts of the tube arranged for the purpose, where the tetrachloride collects, whilst the accompanying more volatile pentachloride passes on. The fused salt conducts excellently, chlorine is evolved, whilst metallic uranium is deposited at the negative pole, in peculiar irregular particles. After the action, the salt, when treated with water, evolves hydrogen, and yields a deep, dark-red solution, leaving a small quantity of uranium as an iron-grey powder. The red solution gives a black precipitate with ammonia, which, however, soon turns green with the evolution of hydrogen. The comparatively small yield of uranium is due to a secondary reaction, resulting in the production of the salt giving the red solution. Uranium oxychloride, UO_2Cl_2 , conducts well, giving off chlorine with the separation of black, crystalline uranous oxide.

The only haloid oxygen compound adapted to these experiments is iodic anhydride; this substance does not conduct in ethereal solutions, but does in absolute alcohol. In this case, however, no gas is evolved, nor any iodine separated; it is therefore assumed that iodic acid and ether, and subsequently ethyl iodate are formed. Aqueous iodic acid is an electrolyte.

The chlorides of sulphur, S_2Cl_2 and SCl_2 , do not conduct. Selenous chloride, Se_2Cl_2 , when perfectly dry, scarcely conducts at all. Selenium tetrachloride sublimates without melting, and in ethereal solution does not conduct; absolute alcohol decomposes it, forming two layers, a heavy, oily, clear liquid, with a pale-yellow supernatant liquid, which reacts acid, and conducts the current moderately well, hydrogen being evolved at the negative pole, but as no selenium separates it is supposed to form some organo-selenium compound.

Tellurium dichloride melts at 160° (uncorr.) to a brownish-black liquid, which is an excellent conductor, with distinct polarisation current. The primary products of electrolysis are obscured by secondary reactions; the tellurium liberated at the negative pole dissolves in the dichloride, whilst the chlorine at the positive pole forms tetrachloride with the dichloride, and also dissolves; ultimately the tellurium and the tetrachloride re-form the dichloride. Tellurium tetrachloride melts at 209° , and is a good conductor; chlorine is evolved, and tellurium is precipitated as a black, flocculent powder; some dichloride forms as a secondary product. Tellurium di-iodide melts at 160° to a black liquid, and is a good conductor; iodine and tellurium are set free. On solidifying, the dichloride forms a lead-grey mass, with metallic lustre where it comes in contact with the glass walls of the vessel.

Manganous chloride melts at a red heat to a reddish-yellow liquid; is a good conductor; chlorine and manganese separate, the latter with indication of crystallisation.

The author, referring to the non-conductivity of water and hydrochloric acid individually, and to their conductivity when mixed,

inclines towards Thomsen's surmise, that the water and hydrochloric acid combine to form the compound $\text{H}\cdot\text{ClH}\cdot\text{OH}$, which on electrolysis breaks up into $\overset{+}{\text{H}}\ \overset{-}{\text{ClH}}\cdot\text{OH}$. The negative complex group may form either chlorine and water, or regenerate hydrochloric acid with the liberation of oxygen. Experimental evidence supports the latter view.

Dry fused ferrous chloride is an excellent conductor. Ferric chloride dissociates on heating, producing some ferrous chloride, and therefore conducts, but absolutely dry ferric chloride in dry ether does not conduct; if, however, the chloride is in the slightest degree moist, or if a few drops of water be mixed with the ethereal solution, it becomes a conductor, and hydrogen is evolved at the negative pole, but no gas comes off from the positive pole; with more water, iron is deposited, but although hydrogen is evolved no ferrous chloride forms, as otherwise, owing to its insolubility in ether, it would be deposited on the negative pole, which is not the case. No chlorine is evolved, as it enters into secondary combination. Ferric chloride is therefore not an electrolyte, but when mixed with water it becomes one. This conversion the author suggests is due to the formation of a compound, $\text{Fe}_2\cdot\text{Cl}_6\text{H}_6\cdot\text{O}_6\text{H}_6$, corresponding to the compound supposed to be formed with hydrochloric acid and water. He supports this suggestion by many arguments, and by demonstrating its accordance with the experimental data. Electrolysis would break it up into the groups $\overset{+}{\text{Fe}_2}\ \overset{-}{6(\text{ClH}\cdot\text{OH})}$, which would fully explain the occurrence of many secondary reactions. Both cobaltous and nickelous chlorides, when fused, conduct the current very well with evolution of chlorine and deposition of the metal in crystalline form.

Ruthenium hexachloride, Ru_2Cl_6 , is infusible and insoluble in ether, somewhat soluble in absolute alcohol with greenish colour; this solution conducts to some extent, but hydrogen only is given off at the negative pole. The aqueous solution of ruthenium hexachloride reacts acid and conducts well, evolving chlorine and hydrogen, and depositing the hydroxide $\text{Ru}_2\text{H}_6\text{O}_6$. Ruthenium tetrachloride is not known in the free state; the dichloride is infusible and insoluble, and could therefore not be used in these experiments, a remark which applies to rhodium chloride, prepared by heating that metal in chlorine, and to the insoluble iridium chloride, Ir_2Cl_6 . Rhodium chloride, Rh_2Cl_6 , was prepared by precipitating sodium rhodium chloride with soda, dissolving the precipitate in hydrochloric acid, &c. This retained some sodium chloride, and when fused at an incipient red heat proved such a good electrolyte and decomposed with such vigour as to take fire. Chlorine is evolved from the carbon positive electrode, whilst metallic rhodium separates at the negative electrode of platinum wire.

Palladic chloride decomposes too readily to be isolated. Palladous chloride is dissolved only in traces by ether, but is soluble in alcohol and in water. Both the latter solutions conduct well, with the separation of metallic palladium. At a red heat palladous chloride fuses, giving off some chlorine, and forming a corresponding amount of subchloride. The fused mass conducts well; the deposited palladium easily forms a thread, which soon extends from pole to pole, and as soon as the metallic circuit is complete the palladium thread glows.

Osmium hexachloride is not known in a free state. Osmium tetrachloride fuses readily, but does not conduct. Osmium dichloride sublimes without melting, but dissolves slightly in ether, more readily in alcohol, and very easily in water, the latter solution soon undergoes decomposition. The ethereal solution does not conduct; the alcoholic conducts slightly; the aqueous readily, and at the negative pole an osmious hydroxide is deposited, which dissolves in hydrochloric acid to a red solution. Platinic chloride, as is well known, decomposes on heating, and is only very slightly soluble in dry ether, nevertheless this solution conducts feebly. The solution of dry platinum chloride in absolute alcohol conducts well, with separation of platinum sponge. The aqueous solution is also an excellent conductor, crystalline platinum separating.

Germanium chloride, GeCl_4 , is a clear, colourless, mobile liquid of sp. gr. 1.887, and boiling at 86° ; it does not conduct either at the ordinary temperature or at the boiling point. D. A. L.

Determination of the Size of the Molecules of Salts from the Electrical Conductivity of their Aqueous Solutions. By P. WALDEN (*Zeit. physikal. Chem.*, **1**, 529—549).—Ostwald (this vol., p. 331) has shown that if m is the molecular conductivity of a dilute salt solution, and v the dilution, dm/dv is of the form $n_1 n_2 \text{ const.}$, where n_1 is the valency of the acid, and n_2 that of the base. The present paper contains further experimental proof of this view, and the results of the examination of a large number of salts.

The first portion of the paper contains the results obtained with magnesium salts. The salts of monobasic acids are found to behave very similarly to salts of monad bases with bibasic acids, the increase in the molecular conductivity with increase in the dilution from 32 to 1024 being between 17 and 20. Salts with bibasic acids give an increase of about double this amount, as was to be expected. The salts of fumaric and maleic acids differ somewhat, the former giving 32.7, and the latter 38.7, and a similar difference exists between the salts of mesaconic and itaconic acids, of which the first gives 30.2, the second 36.5. From this a similar structure may be argued for fumaric and mesaconic acids on the one hand, and for maleic and itaconic acids on the other. The salts of the tribasic citric, and aconitic acids form total exceptions from Ostwald's rule, and the tetrabasic ferrocyanide gave a number which is somewhat low.

In addition to the salts of magnesium, a number of other salts were examined. Potassium ferricyanide gave numbers which show the acid to be tribasic, so that the formula should not be doubled. Barium dithionate gives evidence of the acid being bibasic, and in the hypophosphite the acid is a monobasic one. Of the three sodium orthophosphates, only the monosodium salt gives a normal value, and the author concludes that it alone is undecomposed in solution. The pyrophosphate also appears to be decomposed in solution, and from the measurements obtained so too are potassium dichromate and sodium pyrosulphite, in the last of which, however, the bibasic character of the acid may be recognised. H. C.

Crystallisation of Salts during the Electrolysis of their Solutions. By S. PAGLIANI (*Chem. Centr.*, 1888, 437, from *Atti. R. Inst. Veneto* [6], 5, 1181—1205).—During the electrolysis of solutions of copper, zinc or ferrous sulphates the salt crystallises on the anode, when this is made from the corresponding metal and does not exceed 40 sq. cm. per ampère. When concentrated solutions are used, the strength of the current at the anode is not the same for the different salts. The maximum value of the strength of current, with which this phenomenon occurs, is, for differently concentrated solutions of one and the same salt, the greater the more dilute the solution is. This value depends also very much on the temperature, as it increases as the latter rises. The strength of the current at the cathode is of no influence.

J. W. L.

Magnetic Properties of Nickel. By H. TOMLINSON (*Phil. Mag.*, [5], 25, 372—379).—A nickel wire is placed in the centre of primary and secondary coils consisting of copper wires surrounded with pipeclay and placed in an air-bath, whose temperature is determined by the resistance of a platinum coil. Similar primary and secondary coils without nickel wire are maintained at a constant temperature and connected in series respectively with the above coils and with a battery. The coils are so arranged that the induced currents neutralise one another when the nickel wire is omitted. In making an experiment, when a fixed temperature is reached, the resistances of the coil are made equal to what they were when cold, and the current in the primary is adjusted and opened and closed until the deflections of a reflecting galvanometer become equal. The magnetising force was finally raised to 18·183 C.G.S. The induced currents were compared with those of an earth-coil rotating on a horizontal axis. It was found that the temperature of maximum permeability is lower the greater the magnetising force, whilst the temperature at which the permeability vanishes is higher the greater the magnetising force. The nickel wire used contained iron. A brass wire coated with pure nickel when heated and placed between the poles of an electromagnet, set itself axially with great suddenness as the wire cooled. The rate of loss of permeability appears to be greatest at a temperature of 300°.

H. K. T.

Recalescence of Steel. By H. F. NEWALL (*Phil. Mag.* [5], 25, 510—512).—A steel wire heated by an electric current in a vacuum and in nitrogen gas showed unaltered recalescence, proving that the phenomenon is not due to chemical action or to occluded gases. Recalescence is also not due, as suggested by Forbes, to unequal conductivity at different temperatures, since a steel wire (0·5 mm. in diameter) hammered out to 0·1 mm. thickness still showed reglow. This conclusion is also borne out by an experiment in which a steel rod was allowed to cool slowly, the temperature of the interior being ascertained by means of a platinum-copper couple. At the moment of recalescence, the galvanometer showed a rise of temperature. Similarly when the rod was slowly heated, a fall of temperature was observed at the moment of darkening. The temperature of darkening is higher than that of recalescence, hence the electromotive

force produced when a flame is moved along a steel wire heated so as to show reglow behind the flame and darkening in front of it.

H. K. T.

Molecular Heat of Solid Compounds. By H. KOPP (*Ber.*, 21, 1880—1882).—The author has already (*Abstr.*, 1879, 769) pointed out that the elements carbon, boron, and silicon form exceptions to Dulong and Petit's law, whilst many compounds do not conform to the laws of Neumann and of Garnier and Cannizzaro, when the specific heats are considered as found for the compounds in the solid state and nearly at the ordinary temperature. It was suggested that as the elements carbon, boron, and silicon obey Dulong and Petit's law at a higher temperature, the same might hold good for compounds. This view is supported by recent experiments made with quartz, which is shown by Pionchon (*Compt. rend.*, 106, 1344) to have the sp. heat = 0.305 at 400° to 1000°; sp. heat at 0° = 0.1737. The mol. heat of silica ($60 \times 0.305 = 18.3$) is nearly the same as those of analogously composed metallic chlorides:— $\text{BaCl}_2 = 18.6$ — 18.8 , $\text{CaCl}_2 = 18.2$, &c. The number 18.3 when divided by 3 gives the average atomic heat = 6.1.

N. H. M.

Heats of Combustion of Fumaric, Maleic, and the Pyrocitric Acids. By W. LOUGUININE (*Compt. rend.*, 106, 1289—1291).—The results obtained by means of the calorimetric bomb were as follows:—

Fumaric acid.....	318.176 cal.
Maleic acid.....	331.702 „
Mesaconic acid	479.063 „
Citraconic acid	477.867 „
Itaconic acid	476.58 „

The difference between the heats of combustion of fumaric and maleic acids is considerable, and it is evident that these acids must differ profoundly in their constitution.

In the case of the pyrocitric acids the differences are small, and it follows that the differences in their constitution must be much less profound than in the case of the first two acids.

Fumaric acid is the true homologue of the pyrocitric acids.

C. H. B.

Heat of Combustion of the Solid Isomeride of Benzene. By W. LOUGUININE (*Compt. rend.*, 106, 1472—1473).—The solid isomeride of benzene obtained by Griner (*Abstr.*, 1887, 1033) was burnt in the form of small pastilles in the calorimetric bomb. Heat of combustion for 1 gram = 10863.9 cal. or for 1 gram-molecule 847384 cal. This value approximates somewhat closely to that obtained for gaseous propargyl (853600 cal.), a result which confirms Griner's supposition that they are of similar constitution, thus: Dipropargyl, $\text{CH}:\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}:\text{CH}$, and the solid isomeride, $\text{CMe}:\text{C}\cdot\text{C}:\text{CMe}$. The heat of combustion of benzene is much lower and its constitution is essentially different.

C. H. B.

Heat of Neutralisation of Ethyl Cyanomalonate, Acetocyanacetate, and Benzoylcyanacetate. By A. HALLER and A. GUNTZ (*Compt. rend.*, 106, 1473—1476).—The heats of neutralisation were determined directly, or by decomposing the sodium or barium derivative with sulphuric acid, which precipitates the ethereal salt.

Ethyl Cyanomalonate.—Heat of neutralisation by barium oxide $+2 \times 15.0$ Cal.; by sodium hydroxide $+15.2$ Cal. These values are higher than the heat of neutralisation of hydrochloric acid and almost as great as that of sulphuric acid. It follows that ethyl cyanomalonate is a strong acid. Its sodium salt is not completely decomposed by sulphuric acid, but equilibrium is established between the acid, the ethereal salt and their respective sodium-derivatives. The barium salt crystallises with 4 mols. H_2O . The heat of dissolution of the anhydrous salt is $+2.4$ Cal.; that of the hydrated salt -4.9 Cal., hence the heat of formation of the solid hydrate from the salt and solid water is $+1.6$ Cal. The heat of dissolution of the sodium salt at 10° is -2.6 Cal.

Ethyl Benzoylcyanacetate.—Heat of dissolution of the sodium-derivative -2.75 Cal. If the solution is mixed with sulphuric acid, the ethereal salt is precipitated, and if sodium hydroxide is added immediately, the precipitate dissolves with development of $+11.2$ Cal. If instead of adding the alkali the liquid is allowed to remain about 10 minutes, the precipitated ethereal salt changes in appearance and properties, with development of $+3.6$ Cal. The heat of neutralisation as determined by treatment with sulphuric acid is $+11.6$ Cal. If the heat of transformation of the ethereal salt is taken into account, it is found that the heat of neutralisation of the crystallised ethereal salt is $+7.85$ Cal. From these results it follows that the acid function of ethyl benzoylcyanacetate is less energetic than that of ethyl cyanomalonate.

Ethyl Acetocyanacetate.—Heat of neutralisation by sodium hydroxide $+10.5$ Cal. The precipitated ethereal salt undergoes a transformation similar to that of ethyl benzoylcyanacetate with development of $+1.75$ Cal. The acid function of this ethereal salt is more energetic than that of the preceding salt.

It is evident that the acidic function of the ethyl salts of substituted cyanacetic acids is comparable with that of formic, oxalic, picric, and tartaric acids.

C. H. B.

Specific Gravity of Aqueous Solutions. By T. GERLACH (*Zeit. anal. Chem.*, 27, 271—358).—In groups of salts containing the same acid and of similar constitution, the specific gravity of solutions of equal molecular concentration (that is, containing an equal number of molecules per unit weight of water) increases with the molecular weight of the dissolved salt. The contraction which occurs during the solution of a solid is generally least for the salts of greatest solubility, but to this there are many exceptions, and in the case of certain ammonium salts, expansion even occurs during solution. The contraction is invariably greater with strong than with weak solutions. The molecular heat of salt solutions is (with the exception of a strong solution of sodium acetate) less than the sum of the molecular heats

of the water and salt separately. This modification of the molecular heat is, as a rule, less with strong solutions than with weak ones. For solutions of equal molecular concentration the amount of the modification increases with the molecular weight of the dissolved salt. The value of the fraction $\frac{1 - \text{sp. heat}}{\text{sp. gr.} - 1}$ increases with increased dilution. The quotient obtained by dividing the specific gravity by the specific heat increases with increase of concentration. For equal molecular concentration this quotient increases with the molecular weight of the salt.

M. J. S.

Molecular Volumes of Aromatic Compounds. By F. NEUBECK (*Zeit. physikal. Chem.*, 1, 649—666).—The molecular volumes of a series of related compounds were determined under different pressures at the corresponding boiling points. The substances thus examined were benzene, toluene, xylene, and their nitro- and amido-derivatives. A series of experiments was made with each compound at pressures varying from 150 to 760 mm., and in each case a curve was drawn with pressures as abscissæ and molecular volumes as ordinates. These curves show that an increase in the pressure is attended by an increase in the molecular volume, so that if the pressure increase from P to ΔP , there will be a corresponding increase of Δv in the molecular volume, but always so that in the units taken Δv is smaller than ΔP ; or, in other words, the molecular volume increases less rapidly than the vapour-tension.

A divergence of the curves as the distance from the axis of ordinates is increased, shows that the difference between the molecular volumes of two compounds becomes greater with rising pressures. But by a comparison of these differences for different pressures, it is seen that those regularities which have been established for one pressure still hold good at any other.

It further appears that the influence which an additional substituting group has on the molecular volume of a benzene compound, depends on the position which it takes up relatively to the group already present. If it takes up a para-position, its influence is about the same as when entering into benzene alone, but it is greater than this in the meta-position, and greater still in the ortho. The assumption that each constituent of a compound has a definite molecular volume is not absolutely correct, and therefore, also, the representation of the molecular volume of a compound as the sum of those of its constituents. Among isomeric compounds, the para have the greatest and the ortho the least molecular volumes, and the difference between those of the para and meta is less than between those of the meta and ortho.

H. C.

Molecular Constitution of Dilute Solutions. By M. PLANCK (*Zeit. physikal. Chem.*, 1, 577—582; compare this vol., p. 780).—In a former paper (*Ann. Phys. Chem.* [2], 32, 499) the author has shown that if in any dilute solution n is the number of molecules of the dissolved substances, n_0 the number of molecules of the solvent, θ_0 the freezing point of the solvent, and θ that of the solution in absolute

temperature, and finally Q_0 the latent heat of fusion of one molecule of the solvent, the lowering of the freezing point of the solution is $\theta_0 - \theta = \theta_0^3 n / Q_0 n_0$. From this expression the value for the molecular reduction of the freezing point may be deduced, $T = M(\theta_0 - \theta) = 1.97 \theta_0^3 M / q_0 n_0 M_0$, where q_0 is the latent heat of fusion and M_0 the molecular weight of the solvent, and M the molecular weight of the dissolved substance. The molecular reductions thus calculated for acetic and formic acids, benzene, nitrobenzene, and water agree with those observed by Raoult.

The author further points out that the expression nM , which should be equivalent to the mass of the dissolved substance, will only be correct as long as that substance possesses the molecular weight M . If combination or dissociation of the molecules originally present take place, then the mass of the dissolved substance becomes generally nM/i , where i is less than unity if combination takes place and greater than unity in the case of dissociation. The introduction of i into the above expression leads to results similar to those obtained by Van't Hoff (this vol., p. 780).

H. C.

Dissociation of Substances Dissolved in Water. By S. ARRHENIUS (*Zeit. physikal. Chem.*, **1**, 631—648).—Exceptions to Van't Hoff's law for osmotic pressure in solutions (this vol., p. 778), in cases where the pressure is greater than it theoretically should be, may be explained on the assumption that the molecules of the dissolved salt have undergone dissociation. In the case of electrolytes, the Clausius hypothesis assumes a partial dissociation of the salt into its ions to have taken place, and could it be ascertained to what extent, it would still be possible to apply Van't Hoff's law for calculating the osmotic pressure.

The author has termed the molecules of an electrolyte which may be assumed to exist dissociated in solution the "active" molecules, and the rest which remain intact the "inactive," and the ratio between the number of active molecules and the sum of the active and inactive, the "activity coefficient," α (Lodge's dissociation ratio). This number is the ratio between the actual molecular conductivity of the solution and the limiting value which it approaches with increasing dilution. α being known, Van't Hoff's coefficient i , the ratio between the osmotic pressure which a substance exercises and that which it would exercise if composed solely of inactive molecules, may be calculated. For i is equal to the sum of the inactive molecules and the number of ions, divided by the whole number of active and inactive molecules. Hence if m is the number of inactive and n that of active molecules, and k the number of ions into which each active molecule separates, then $i = (m + kn)/(m + n)$ or since $\alpha = n/(m + n)$ then $i = 1 + (k - 1)\alpha$. The other method of calculating i is that given by Van't Hoff, and consists in dividing the observed molecular reduction in the freezing point of water produced by the substance by 18.5.

A table is drawn up of the values of i for a large number of salts calculated by both the above methods, and it shows a general agreement between the two. From this the author argues the truth of his

assumption of the dissociation of substances dissolved in water, on which the calculation is based. He concludes that Van't Hoff's law holds for all substances, the exceptions being due to dissociation, and that dissociation of electrolytes always takes place in solution, increasing in amount with the dilution until in an infinitely dilute solution only active molecules occur.

In the second portion of the paper he enters into a discussion of the other properties of solution with reference to their bearings on the above views.

H. C.

Hydrates of Gases. By H. W. B. ROOZEBOOM (*Compt. rend.*, **106**, 1292—1293).—A claim for priority over de Forcrand and Villard (this vol., p. 644). The author's papers may be found in *Rec. Trav. Chim.*, vols. **3**, **4**, **5**, and **6**.

C. H. B.

Hydrates of Hydrogen Sulphide and Methyl Chloride. By DE FORCRAND and VILLARD (*Compt. rend.*, **106**, 1402—1405).—The apparatus employed for the determination of the composition of these compounds consists of a strong bulb of 150 c.c. capacity, into the neck of which is fused a vertical tube reaching to the bottom of the bulb. Attached laterally to the neck of the bulb is a bent tube with a bulb of 15 to 16 c.c. capacity, terminating in a tube drawn out to a point. 40 to 50 grams of mercury and 0.2 to 0.6 gram of water is introduced into the side bulb and some mercury is poured into the larger bulb until it closes the opening of the vertical tube. A current of the gas is passed into the apparatus until all the air is expelled; the drawn-out end of the bulb is sealed, and the passage of the gas is continued until the apparatus is filled with gas at a pressure of a few centimetres above that of the atmosphere. It is then cooled to 0° and the pressure of the gas measured. A part of the side bulb is now cooled below 0°, and crystals of the hydrate begin to form. Mercury is poured down the vertical tube, from a quantity previously weighed, in order to maintain the pressure, and the mercury in the side bulb is repeatedly agitated in order to break up the layer of crystals. When the crystals have become quite dry, the absorption of gas ceases, and after the height of the mercury has remained constant for several hours, the pressure is readjusted. The volume of gas absorbed is measured by the quantity of mercury which has been added. The apparatus is now placed in a warm room, when the crystals melt with evolution of gas, which expels the mercury through the vertical tube. The side bulb containing mercury and water is detached and weighed, then dried and weighed again, the loss in weight giving of course the quantity of water.

In this way it was found that the hydrate of hydrogen sulphide has the composition $\text{SH}_2 + 7\text{H}_2\text{O}$, and the hydrate of methyl chloride the composition $\text{MeCl} + 9\text{H}_2\text{O}$.

C. H. B.

Hydrate of Methyl Chloride. By DE FORCRAND and VILLARD (*Compt. rend.*, **106**, 1357—1359).—The following values were obtained for the tension of dissociation measured from 760 mm. :—

Temp. . . .	0.0°	0.5	0.9	2.4	4.8	6.5	8.0	10.5
Pressure. .	—449	—426	—411	—344	—203	—73	+6.5	+336
VOL. LIV.							3 0	

Temp.....	12.5°	14.35	14.5	14.9	15.5	16.2	17.5	19.5
Pressure..	+648	1065	1083	1208	1368	1513	1920	2382
Temp....	20.1°	20.4	21.0	22.0				
Pressure..	2750	2927	2996	3134				

The tension is equal to 760 mm. at +7.3. Up to 20.6 only water and crystals of the hydrate are present, but at this temperature some of the methyl chloride separates in oily drops on the surface of the water, although some crystals of the hydrate remain undecomposed. At 20.9 the crystals are entirely decomposed and the drops of methyl chloride volatilise. The curve representing the tensions of the hydrate and Regnault's curve for the tension of methyl chloride intersect at about 20.5.
C. H. B.

Osmose through Precipitated Diaphragms. By G. TAMMANN (*Ann. Phys. Chem.* [2], **34**, 299—315).—If a solution is separated from a portion of the same solvent by a precipitated diaphragm which does not allow the substance in solution to pass through it, then the osmotic coefficient of the solution is represented by the quantity of the solvent which flows through unit area of the diaphragm in unit time. If at the temperature of observation, the vapour-pressure of the dissolved substance is zero, the values of the osmotic coefficient of the solutions, with similar diaphragms, will be proportional to the amounts by which their vapour-pressures are lowered. From this it would follow that solutions having equal osmotic coefficients would also have equal vapour-pressures. The author has been for some time engaged on a series of experimental investigations with a view of testing the truth of this relation, and in the meantime Van t'Hoff has shown (this vol., p. 778), from thermodynamic considerations, that no osmose can take place between solutions which have equal vapour-pressures.

The author found that Pfeffer's method of observation (*Osmotische Untersuch.*, 1887, 15) was not trustworthy, owing to the liability to change in the state of the diaphragm. The method employed in the present research is based on the observation of phenomena depending on changes in refrangibility of portions of the solutions on opposite sides of the diaphragm, due to changes in density produced by osmotic currents.

A large number of diaphragms were tried, but the only satisfactory ones consisted of ferrocyanide of zinc and ferrocyanide of copper formed by the contact of salts of zinc or copper with solutions of ferrocyanide of potassium.

Some of the experiments seemed to indicate that the vapour-pressure of a solution of potassium ferrocyanide is increased when a portion of zinc ferrocyanide is dissolved in it.

Both the diaphragms were found to be permeable to potassium chloride and nitrate, but impermeable to the sulphate.

The copper ferrocyanide diaphragm was also found to be permeable, against the direction of the osmotic current, to carbamide, ethyl and propyl alcohols, and ethyl acetate; and impermeable, against the direction of the current, to barium chloride, ammonium sulphate, cane- and grape-sugar, salicin, isobutyl alcohol, and chloral hydrate.

From experiments on a number of mixtures, the author found that

in general the lowering of the vapour-pressure was sensibly equal to the sum of the amounts by which the vapour-pressures of the constituents would be lowered separately, but there were some decided exceptions to the rule, namely, the lowering of the vapour-pressure of mixtures of ammonium sulphate and copper sulphate, barium chloride and copper chloride, and potassium chloride and copper chloride was found to be greater than it would be if this relation held good. The author illustrates the results of his experiments by a number of isosmotic curves, in which the ordinates represent the molecular concentration of the solution of potassium ferrocyanide, and the abscissæ the molecular concentration of the salt compared with it. In the case of simple metallic salts, he finds that these curves agree with similarly drawn curves of equal vapour-pressure, proving the truth of the law that solutions which have equal osmotic coefficients have equal vapour-pressures.

The isosmotic curves for the different organic substances (dissolved in solutions of copper sulphate) investigated were found to agree very closely, and their deviations from a mean curve representing the whole of them were within the limits of experimental error.

This seems to show that the osmotic coefficient does not depend on whether the substance in solution is a solid or a liquid, but this is not true for the vapour-pressure, and therefore a solution of potassium ferrocyanide cannot have the same vapour-pressure as isosmotic solutions of ethyl ether, ethyl alcohol, and propyl alcohol. If then two solutions are isosmotic the molecular motions of the common solvent must be equal, and if the substance in solution is a solid the vapour-pressure may be taken as a measure of the molecular motion, so that isosmotic solutions of such substances have equal vapour-pressures. If a liquid is dissolved in a liquid, then at the freezing point the vapour-pressure of the solution and the solidified solvent will certainly not be equal, but the molecular motion of the solvent must be the same for the solid and liquid portions, and therefore isosmotic solutions of liquids must have equal freezing points.

If the lowering in the freezing point and in the vapour-pressure of a solution are proportional to the percentage of substance in solution, the quotient of the molecular lowering of the freezing point of two solutions must be equal to that of their isosmotic concentration, and the author gives a table comparing the latter quotients obtained from his own experiments with the quotients of the molecular lowering in the freezing points according to Raoult (*Compt. rend.*, **94**, 1517), the values for potassium ferrocyanide being taken as the standard of comparison, and the agreement appears to be sufficiently close to justify the conclusion.

G. W. T.

Constitution of Solutions. By F. RÜDORFF (*Ber.*, **21**, 1882—1885; compare this vol., p. 342).—Diffusion experiments made with 6 per cent., 10 per cent., and 13·5 per cent. (saturated) solutions of potassium copper sulphate show that the decomposition of the double salt does not depend on the degree of concentration, the decomposition being nearly the same in each case. If, however, coarsely powdered salt is put into the diaphragm so that the solution

will remain concentrated, or nearly so, a different result is obtained; the diffusate contained to 100 parts of copper an average of 183·9 of potassium instead of 287·0, 273·9, and 280·8, obtained as means of the three other experiments. With solutions of ammonium magnesium sulphate, potassium chrome alum, ammonium manganese sulphate, and ammonium cupric chloride, similar results were obtained.

N. H. M.

Absorptive Power of Colloid Substances. By J. M. VAN BEMMELEN (*Landw. Versuchs-Stat.*, **35**, 69—136). See p. 985.

Rate of the Reaction between Marble and Hydrochloric Acid. By J. J. BOGUSKI (*Zeit. physikal. Chem.*, **1**, 558—564).—The author finds that experiments conducted at different temperatures cannot be compared on account of the change in the surface of the marble. At a temperature of about 19—21° the rate of the reaction is proportional to the concentration of the acid, at 0° it increases more slowly, at 50° more rapidly than the concentration. Thus if v be the rate of the reaction and y the concentration, at 20° $v = ky$, at 50° y must be raised to some power greater, at 0° to one less than unity.

Much appears to depend on the viscosity of the solution. Thus the reaction is far less rapid with hydrochloric acid dissolved in glycerol than in water, and less rapid in water than in alcohol.

H. C.

Rate of the Reaction between Iceland Spar and Acids. By W. SPRING (*Bull. Soc. Chim.*, **49**, 3—11).—The rate of the reaction between Iceland spar and acids was determined by the same method as that described in the case of marble (Abstr., 1887, 882). The volume of acid employed was such that the reaction ceased after the evolution of 522 c.c. (760 mm., 15°) of carbonic anhydride. The spar was examined (1) in the direction of cleavage, (2) in a direction parallel with, and (3) in a direction perpendicular to the principal axis, with the following results:—

(1.) All surfaces of cleavage dissolve with the same rapidity when treated with 10 per cent. hydrochloric acid at 15°, 35° and 55°, other conditions being equal. Between 15° and 35° the rapidity of solution varies in proportion to the concentration of the acid, but at 55° the rapidity diminishes more quickly than the concentration. At each of the three temperatures, after the evolution of 350 c.c. of carbonic anhydride, the rapidity of solution diminishes so quickly that practically the reaction may be considered as null after the evolution of 400 c.c. at 15° and 35°, and 425 c.c. at 55°; the concentration of the acid is then 2·34 per cent. and 1·86 per cent. respectively. Iceland spar is only attacked with extreme slowness by 2 per cent. hydrochloric acid. For each of the three temperatures, the rapidity of solution is less than in the case of marble, and the difference increases slowly, but regularly, with the temperature. The law of solubility is the same for Iceland spar as for marble, the temperature being the same, but in the case of the former the reaction does not commence until the hydrochloric acid has attained a concentration of 2·34 per cent. Unless special precautions are taken, the rapidity of the reaction appears to

reach its maximum only after the production of 50 to 75 c.c. of gas, owing to absorption of gas by the liquid. The rapidity of solution is the same in hydrochloric, nitric, and hydriodic acids of equivalent strengths, but in hydrobromic acid the rapidity of solution exceeds that in the above-named acids in proportion to the concentration, so that the difference tends to become null as the concentration diminishes.

(2.) The rapidity of the reaction with faces cut parallel to the principal axis is, at 15°, practically the same as with faces of cleavage, but at 35° it is 1.23 times, and at 55° it is 1.28 times greater on the average, so that above a certain temperature the rapidity of solution no longer diminishes in proportion to the temperature.

(3.) With faces cut perpendicular to the principal axis, the rapidity of solution is greater than in the preceding case. At 15° the rapidity diminishes in proportion to the concentration, at 35°, and especially at 55°, the rapidity diminishes very slowly until about one-tenth of the theoretical quantity of gas has been evolved, the rate of solution then decreases more rapidly, and finally, after about one-fifth of the acid is used up, becomes proportional to the concentration of the acid. The rapidity of the reaction increases, therefore, during a certain time, in spite of a decrease in the strength of the acid, just as is the case with marble, and this phenomenon is not in any way due to the absorption of gas by the liquid at the commencement of the reaction.

From a comparison of the results obtained in the last two cases, it seems that a certain relation exists between the chemical activity of a substance and its optical elasticity in a given direction.

F. S. K.

Rate of Formation of Ethereal Salts. By N. MENSCHUTKIN (*Zeit. physikal. Chem.*, 1, 611—630).—The determination of the rate of formation of acetates from different alcohols in benzene solutions, gave the following comparative values for the constants of velocity, that of methyl alcohol being taken as 100 :—

Primary Alcohols.

Methyl alcohol	100.0	Octyl alcohol	35.8
Ethyl „	47.9	Tetradecyl alcohol	27.6
Propyl „	45.6	Hexdecyl „	25.5
Butyl „	44.1	Octodecyl „	23.2
Isobutyl „	38.1	Myricyl „	16.5
Heptyl „	37.3		

Unsaturated Primary Alcohols.

Allyl alcohol	27.2	Benzyl alcohol	26.6
α -Methylallyl alcohol. .	25.2		

Secondary Alcohols.

Dimethyl carbinol	14.1	Methyl hexyl carbinol	8.7
Methyl ethyl carbinol . .	11.6	Methyl allyl „ . .	6.1

Tertiary Alcohol.

Trimethyl carbinol, 0.8.

From this table it will be seen that the values for the constants are greatest for the primary alcohols, and that again among these they are greater for the saturated than for the unsaturated alcohols. In homologous series an increase in the molecular weight is found to be attended with a decrease in the value of the constant, which decrease is, however, not the same for each CH_2 -group added.

The effect of varying the solvent in which the reaction takes place is to materially alter the value of the constant. Thus putting the value of the constant for isobutyl alcohol in benzene solution as unity, we get in xylene solution 1.37, and in hexane solution 2.18, and with the value for isopropyl alcohol in benzene as unity, we get in xylene 1.25, and in hexane 2.07.

H. C.

Equivalents of the Elements. By DELAUNEY (*Compt. rend.*, **106**, 1405—1407).—If the equivalent of hydrogen is taken as unity, the equivalents of the other elements are represented by the expression $\frac{N}{3}\sqrt{5^2-n^2}$, in which N and n are whole numbers, the value of n being 0, 1, 2, 3, or 4. The calculated numbers agree fairly well with the actual determinations. The elements may be divided into groups or families according to the values of n , but the same element may fall into two or even three families. The omission of $\frac{N}{3}$ merely changes the unit of equivalence, and hence only the simplified expression $\sqrt{5^2-n^2}$ need be considered.

The author imagines the existence of a primitive molecule composed of 5 atoms revolving at different distances round a central atom after the manner of planets round a sun. If such a system is penetrated by a group of atoms, all tangent to one another, the opposite directions of their motions will give rise to a stress which will result in an agglomeration of the atoms.

C. H. B.

A Certain Atomic Hypothesis. By K. PEARSON (*Cambridge Phil. Trans.*, **14**, 71—120).—This paper is one of very great interest to chemists, but in its original form would probably repel them by its masses of mathematical formulæ. The author points out that the view which regards the physical universe as a continuous medium, is rapidly displacing the old molecular hypothesis. Certain portions of this medium are supposed to be differentiated from the rest, to be indestructible, and to possess internal energy and also external energy (of translation). Vortex atoms are an example of this. This new point of view reduces all the phenomena of physics to problems in hydrodynamics, and the explanation of all mutual actions of atoms is sought in the motion existing in the medium. The constant recurrence of the same types of equations in all branches of physics thus receives a new meaning. Great light has been thrown on this view by the experiments of Bjerknæs of Christiania, who showed that spherical substances oscillating in a fluid medium act like magnetic molecules with axes in the directions of oscillation, whence he gave the name of hydromagnetism to the phenomena. Neglecting rotations, the motion of an atom will consist of vibration and translation. If the vibra-

tions are of the same kind as those to which light is due, the velocity of translation due to planetary motion in space may be neglected in comparison with the rate at which a point on the surface of an atom is capable of moving. In a former paper (*Quart. Journ. Math.*, **20**, 77) the author has shown that the expression for the energy of a system of two atoms contains four significant terms. The first involves only vibrations, perhaps analogous to those which produce heat and light. The second involves only oscillations, perhaps analogous to those which produce magnetic phenomena. The third and fourth involve both vibrations and oscillations, and may possibly give rise to phenomena involving relations between light and magnetism. In the first place, the author supposes no "hydromagnetic" oscillations to exist, so that only vibrations have to be considered. For simplicity in the mathematical treatment he supposes the atoms to be spherical and the vibrations to consist of pulsations of the entire surface.

When the atoms are free, these pulsations will consist of a definite number of beats of fixed periods, and as there seems reason to believe that a gas at low pressure, and not too hot, gives only one bright line, it is probable that each atom has only one period of free vibration.

The constraint due to the approach of other atoms would ultimately give a continuous range of beats corresponding with the observed change in the spectrum of a rare gas gradually changing to a solid. A molecule may consist either of like or unlike atoms, and its pulsations may be either free or forced, but those of its constituent atoms must necessarily be forced. The free pulsations of a molecule may have no apparent relation to those of its atoms, just as the spectrum of a compound gas has no obvious relation to the spectra of its constituents, and a substance consisting of like atoms may exist in various molecular states, each with its own spectrum.

In the hydrodynamical investigation of these pulsating spherical atoms, the author assumes the existence of a velocity-potential, and, therefore, that there is no rotational motion of the ether outside the atoms. As the surface-condition, he assumes the velocity of the fluid normal to the surface of the atom to be equal to the normal velocity of the surface. He then considers the case of 2 atoms, and the resulting equation admits of solution in the ordinary manner in a series of zonal harmonics. The form of the expression thus obtained suggests the generalisation of considering, instead of simple pulsations, polar vibrations symmetrical about the line of centres. These would be the forced vibrations in one atom produced by free pulsations in the other. The kinetic energy of the fluid is next determined. To obtain the kinetic and potential energies of an atom, some hypothesis has to be made about its nature, and the author makes the assumption that it is a solid, elastic sphere. A curious result then comes out. The vibrations of the fluid are found to have the effect of increasing, by a definite amount, the quantity expressing the mass of the atom, so that if the atoms were without actual mass, they would still have an apparent mass due to the vibrations of the fluid. The same would apply to a linear motion of atoms in the ether, but in either case, in order to produce the vibrations, the atoms or their surfaces must possess potential energy. An atom might, therefore, be the one im-

material thing in the universe, consisting of a perfect vacuum (even as to ether) in the boundary of which potential energy in some manner resides.

Suppose, now, that the distance between the atoms is so great that they have no mutual action. Then we can determine the free vibrations produced by a "single pole" disturbance, if the atom is disturbed, and then left to vibrate freely in the ether. Assume the free vibration to be a pulsation, and it will correspond with the single bright-line vibration. Then it appears that if the actual mass of the atom is not zero, the potential energy resident in the surface must contain a factor determined by the mechanical structure of the atom, depending on its elasticity, for example. The period will, therefore, probably depend on the density, or on the radius, or on both.

Now, according to Lockyer (*Studies in Spectrum Analysis*, 143), "There is a noteworthy connection between the atomic weight of metalloids and the region of the spectrum where their lines appear under similar conditions." A careful examination of the position of the single bright lines and of the atomic weights of different substances might thus throw some light on the mechanical structure of atoms.

It should be noted that the natural pulsations of an atom are of greater importance than its other free vibrations, because the latter will be about different sets of poles in different atoms, so that when the atoms after collision pass beyond the sphere of mutual action, these vibrations will not have a common direction as in the case of the pulsations, so that they will produce less effect on the ether.

The free vibrations of a pair of mutually acting atoms are next considered, and it is found that a new set of periods is introduced which are functions of the distance between the atoms. If this distance is great, these periods do not differ much from that of free vibration of either. There will thus be a number of periods grouped about the natural periods. If they correspond with light vibrations, we should expect the spectrum lines to spread out into bands when the atoms of a gas are brought nearer together. When the distance becomes very small, the vibrations of any pair will differ considerably from the free vibrations of either, and, as they depend on the distance, they will vary from pair to pair, so that, ultimately, there will be a continuous spectrum. Again, if a chemical combination consisted of two atoms in close union, we should not expect the spectrum to consist of their separate spectra superposed.

In the case of three or more atoms, the consideration of polar vibration presents great difficulties, so the author here considers pulsations only. He arrives at the conclusion that a gas composed of molecules, each containing three different atoms, will, when at low pressure and not too high temperature, have a spectrum consisting in part of two bright lines, one nearer to the violet and the other nearer to the red than any bright line due to the component atoms pulsating freely. He finds that the more nearly the pulsation periods of two atoms agree, the more intense will be the vibrations of the molecule formed by their union.

For a molecule composed of three atoms, of which two only are alike, he finds that there will be two bright lines equidistant on each

side of the line due to the like pair, and one bright line farther from this line than the original line due to the unlike atom.

For a molecule consisting of three similar atoms, there will be two bright lines nearer to the violet, and one nearer to the red than that due to the atoms, and if the atoms are equidistant, the two former will coincide.

For a molecule consisting of two atoms of different periods there will be two bright lines, one nearer the violet and the other nearer the red than the originals.

For a molecule consisting of two atoms of equal periods, there will be two bright lines, the lower further towards the red than the upper one towards the violet.

In the case of three similar and equidistant atoms, the line nearer to violet will be brighter than in the case of two atoms. This suggests experiments on spectra of the same element in different molecular conditions, such as oxygen and ozone.

It is also shown that the dissociation of a diatomic molecule ought to be accompanied by a greater generation of heat, the nearer the single bright line is to the violet end of the spectrum; for example, the fundamental line of hydrogen should be nearer the violet than that of carbon.

The author then proceeds to consider a number (p) of mutually reacting atoms of different kinds, and he shows that the spectrum of the combination may be deduced when the single bright lines given by the component atoms are known.

It is shown that the sum of the squares of the periods of pulsation (whether under mutual action or free) is always constant, and as a special case, if, owing to the effect of pressure or temperature, an element gives p spectral lines instead of a single bright line, then the sum of the squares of the periods corresponding with the p bright lines is equal to p times the square of the period corresponding with the single bright line.

In calculating a theoretical spectrum, the author points out that we must not expect always to have as many bright lines as there are atoms in the combination, as some of them may fall in the invisible portions of the spectrum.

Since the periods of a combination depend on the central distances between the component atoms, a combination of atoms oscillating about a mean position would give a fluted spectrum.

Again, if there are a great number of atoms at each instant within the sphere of mutual action, there will be a great number of pulsations corresponding with all the central distances, and the complexity of these lines may make them appear like bands, and so give rise to a fluted spectrum. This would be more or less the case for an element not in a molecular state, and the atoms of which come very close together.

By considering the number of atoms within a sphere of given radius, it is easily seen that if the spectrum of an element has, say, 300 lines at the ordinary pressure, it will have not more than seven lines at $1/64$ of the ordinary pressure, and before the pressure falls to $1/125$ it will only give one line, supposing the temperature to remain constant, and that the ultimate atoms, supposed uniform, have only

one free pulsation. This appears suggestive in relation to the spectrum of iron. It is assumed, of course, that the ultimate atoms of the element are uniform and have only one free pulsation.

The difference between the spectrum of a mixture and of a chemical combination introduces the idea of atoms united into groups. The forces between the constituent atoms are called *chemical forces*, those between groups or molecules at small distances *molecular forces*, at great distances *gravitational forces*.

To see what light the theory throws on these three kinds of forces, the author considers the expression for the total kinetic energy of atoms and fluid, and supposes only pulsations without polar vibrations. He also assumes that the linear velocities of the atoms are not of a magnitude comparable with those supposed to produce magnetic phenomena.

Chemical Forces.—The consideration of two atoms in the same molecule, then, leads to the result that the atomic force between them must vary, partly as the inverse cube, and partly as the inverse fifth power of their central distances. For molecular union, the force must be attractive, which leads to the condition that the product of the potential energy coefficient by the intensity of free pulsation must be greater for the atom having the greater free period. When the central distance is large relatively to the atomic radii, the forces of chemical combination vary as the inverse cube. For two equal atoms the law is the same, provided the pulsations are of equal intensity; if not, the force is made up of the inverse square, cube, fourth and fifth powers of the distance, the second always repulsive, and the others attractive or repulsive, and it is found that unless a decrease in the period denotes a decrease in the atomic radius, the force of chemical combination will increase as the periods decrease, so that a molecule giving lines in the violet will be more stable than one giving lines in the red.

The author has not been able to determine whether the equilibrium in a diatomic molecule is statical or whether one atom describes an orbit about the other. Whether the former is possible except for atoms in contact depends on their internal structure, about which we know nothing. In the case of two unlike atoms, or of two like atoms having equal pulsation amplitudes, describing a relative orbit, the latter is not in general a closed curve, so that permanent union would be impossible. The author thinks it probable that the nature of the equilibrium may depend on the molecular state of a body. For example, the molecules of a rare gas may be in dynamical equilibrium, describing orbits about each other, while those of solids may be in statical equilibrium.

Consider p unlike atoms in a molecule. Let the chemical intensity be defined as the product of the potential energy coefficient into the intensity of free pulsation, and let the difference of the chemical intensities divided by the difference of the squares of the periods be called the chemical coefficient. Then it is found that the atoms will attract, and can therefore form a molecule, if this coefficient is positive, whilst if it is negative they will repel. When a_1 and a_2 are the radii of two atoms, and τ_1 and τ_2 the potential energy coefficients, the force between the two atoms is found to be—

$$\frac{\text{Chemical coefficient}}{(\text{Central distance})^3} \times \frac{64\pi^4 a_1^2 a_2^2}{\tau_1 \tau_2},$$

which the author calls—

$$\frac{\text{Chemical affinity}}{(\text{Central distance})^3}.$$

A knowledge of the chemical affinity for every pair of p atoms would enable us to determine the possibility of the p atoms uniting to form a molecule, and also the stability of the molecule if it could be formed.

Suppose a third atom to be added to a pair already in combination. Let $2\pi/\nu_1$ and $2\pi/\nu_2$ be the periods, and I_1 and I_2 the chemical intensities of the combined atoms; and let $2\pi/\nu_3$ and I_3 represent the same quantities for the third atom. Suppose ν_1 greater than ν_2 , and, therefore, I_1 less than I_2 . Then the following results are obtained:—
Case I, ν_3 greater than ν_1 .

Combination is possible if I_3 is less than I_2 or I_1 , as the third atom is attracted by both the combined atoms. If I_3 is greater than either I_2 or I_1 combination is impossible, as the third atom is repelled by both. If I_3 lies between I_2 and I_1 the third atom is attracted by one and repelled by the other. Let A_{12} be the chemical affinity between the two combined atoms, A_{13} and A_{23} those between the combined and uncombined, and let γ_{12} , γ_{13} , γ_{23} be the distances between the atoms. Then if $-A_{13}/\gamma_{13}^3$ is less than A_{23}/γ_{23}^3 the third atom will remain in the combination. If A_{12}/γ_{12}^3 is less than $-A_{13}/\gamma_{13}^3$ the first atom will be turned out of the combination and the third substituted for it, forming a new stable diatomic molecule. If A_{12}/γ_{12}^3 is greater than $-A_{13}/\gamma_{13}^3$ the third atom will, as in the last case, attract the second and repel the first, but the first will remain in the combination, so that the molecule will contain two mutually repelling atoms united by a third atom attracting both of them, so that the result will be an unstable molecule. Molecules of this character give rise to unstable and explosive compounds.

Other cases in which ν_3 lies between ν_1 and ν_2 , and in which it is less than either, give results of the same character. The investigations appear to indicate that it would be impossible for an element in its dissociated state, that is, with its atoms not in molecular union, to break up a diatomic compound in such a manner that all these elements should be dissociated. The law indicated in this case is easily generalised.

The author points out that the results which have been considered show that his theory would make all questions of chemical combination or decomposition one simply of calculation, if the free pulsation of every elementary atom could be observed, and chemical intensities and affinities tabulated.

Molecular Forces.—In a gas at ordinary pressure and density the atoms in each molecule may be considered to be executing forced pulsations under the influence of the other atoms of the same molecule, but independently of the atoms in other molecules. On this supposition the author shows that the force between two molecules will vary partly as the inverse square, and partly as the inverse fifth power of

their central distance. The latter will always be attractive; the former will also be attractive provided like atoms in like molecules are pulsating in the same phase, and also for certain other relations between the phases, which, however, are of too arbitrary a character to be at all probable. Now a solid always gives a gas composed of like molecules, so that the cohesion of a solid must be due to molecular and not to chemical forces, and therefore it is impossible to suppose the forces between molecules partly repulsive. Thus it seems probable that like atoms in like molecules must really be pulsating in the same phase, and this receives independent confirmation from considerations founded on the undulatory theory of light; the author, therefore, assumes it to be true.

Every term of the intensity of this attractive force contains as a factor the reciprocal of the square of some period of the molecular pulsations. Let $2\pi/n$ be the period of a molecular pulsation, a the radius of an atom, then it is reasonable to assume that a^4n^2 will increase with n , and in this case it follows that the molecular forces will be greatest for substances which give bright lines nearest to the violet, so that their force of cohesion, or toughness, when in a solid state will be greatest, or the toughness of pure metals should be in the same order as the rates of vibration corresponding with their single bright lines.

The conclusion that like atoms in like molecules must be pulsating in the same phase is found to apply also to free atoms, or atoms which are not in molecular union with other atoms, but when the free pulsation is altered to a forced one, the phase may be changed, it being then required only that the alteration should be a function of atomic radius / central distance, and should vanish with this quantity.

When a substance is under constant conditions, the chemical affinity cannot be supposed to vary greatly from molecule to molecule, so that not only the phases, but the amplitudes of the atomic pulsations of the molecules must be very much alike for the corresponding atoms of different molecules.

Although the action of a single atom on another vanishes when their distance is great in comparison with the atomic radii, nevertheless a great number of atoms may produce a considerable total effect on a single atom, even when at comparatively great distances from it, provided their effect is to produce a wave in the ether of the same, or nearly the same, period as the free period of the single atom.

The amplitude of the free pulsation, or, in the case of an atom in a molecule, the amplitude of the forced pulsation, not differing greatly in period from that of the free pulsation, will be most affected. This change of amplitude will affect the chemical intensity of the atom, and therefore the chemical affinity of each pair of atoms, which explains the physical and chemical effects of waves of different periods (chemical, light, and heat waves), as they alter the chemical intensities of the atoms, the chemical affinity between the atoms of the same molecule, and also the molecular forces acting between the different parts of the substance.

If magnetism and electricity consist in oscillations of the ultimate atoms they will not affect their pulsations directly, but they will do so indirectly by altering their distances. When, however, atoms are

pulsating freely, alterations in the atomic distances have no effect on the pulsations, so that according to the author's theory magnetism and electricity should have no effect on the spectra of completely dissociated gases.

It should be noted that the state of a substance will not be fully defined by the nature of the atoms and of the manner in which they are united to form molecules, for the condition of a molecule at any moment will be a function of the ether disturbance in its neighbourhood, so that the physical and chemical properties of a body will depend on the state of the neighbouring ether. If the exact nature of the ether disturbance in the neighbourhood of a molecule at any moment could be ascertained, every property of the molecule could be determined without reference to other molecules.

Gravitational Forces.—The motion of translation, or oscillatory motion of two molecules, gives rise to a force of magnetic character between them. Now it is difficult to imagine any effect from the rotation of a spherical molecule in a perfect fluid, and even if the molecules are ellipsoidal it is found that the effect of their rotation is not to produce a mutual action of the nature of gravitation. The explanation of gravitation must therefore be sought in the pulsations.

The author finds that if the law of gravitation holds for all atoms, then every atom must have at least one pulsation of common period and phase with every other. He also arrives at the conclusion that all the atoms in the universe must have begun to pulsate at the same moment. He finds that the force of gravitation is not exactly $\text{mass}/(\text{distance})^2$, but a certain function of the constitution of the two bodies divided by the square of the distance. In solid substances this may be almost exactly equal to the product of their masses, but in some cases it may vanish, as for instance in the case of two gases vibrating freely and having no common period of pulsation. This would not open the possibility of a substance being without weight, for since all solids and liquids give continuous spectra they must have pulsation periods in common with one or more of the periods of every other substance. It would, however, lead to the result that the density of a substance if measured by the attraction exerted between it and another substance, would vary to some extent according to the substance selected as a standard of comparison. As a matter of fact very different results have been obtained by different methods for the mean density of the earth, the values ranging from less than 5 up to 6.6, and even in Baily's experiments the average mean density obtained from experiments with balls of one substance on the torsion rod, differed from the results obtained when balls of another material were used.

The author shows that change in the atomic conditions of a substance need not affect the weight. In the cases which he considers it is found that the conditions for the weight to remain unaltered lead to relations previously proved to be true. The theory, however, leads to the result that the weight of a substance must be increased, though the increase may be very minute, by absorption of light or heat, as the effect of this will be to increase the amplitude of the pulsations. These discrepancies with what are considered well established physical facts may indicate that the pulsations are insufficient alone to explain gravitation, and that this may depend also on the shape of the atoms,

and on the nature of their vibration, or more probably on the nature of the medium in which they are vibrating. If, for example, the ether is not a perfect fluid, there may be something of the nature of skin-friction between the atoms and the ether, and in that case it is possible that gravitation may be due to rotation of the atoms.

The theory discussed in this paper is certainly one of great interest and suggestiveness, and appears to throw great light on many problems lying on the borderland of chemistry and physics. The few discrepancies which have been noted are not surprising, as practically nothing is known about the nature of the ether. Some of the phenomena of light appear to lead to the conclusion that it is a perfect fluid, as assumed in the preceding paper, whilst others appear to require it to have the properties of a very elastic solid.

G. W. T.

Note.—Sir William Thomson has pointed out (*Baltimore Lectures on Molecular Dynamics*) that there is no contradiction involved in supposing the ether to act like a perfectly elastic solid for vibrations executed in the 100 or 1600 billionth of a second, and yet to be highly mobile to substances moving at a rate of, say, 20 miles a second, and points out as an illustration that a tuning-fork can be made of Burgundy pitch when the period is a small fraction of a second, yet a bullet will, by its own weight, penetrate several inches into it in six months.

It should be borne in mind that, as stated on page 903, the spherical form of the atoms is assumed simply to facilitate the mathematical analysis, and the author, in a letter to the abstractor, points out that if the atoms are of any other shape, provided they are capable of changing their external form, and especially their size, their treatment as pulsating spheres will probably give a first approximation to the true theory.

G. W. T.

Lecture Experiment. By B. F. OETTEL (*Chem. Zeit.*, **11**, 1601).—A small heap of finely powdered potassium chlorate supported on a piece of filter-paper on a tripod is saturated with a solution of phosphorus in carbon bisulphide. As soon as the latter evaporates, the mass explodes with loud report and clouds of smoke.

D. A. L.

Inorganic Chemistry.

Relative Values of Atomic Weights of Hydrogen and Oxygen. By J. P. COOKE and T. W. RICHARDS (*Amer. Chem. J.*, **10**, 191—196).—It was suggested by Rayleigh (this vol., p. 643) that the balloon used for weighing hydrogen (this vol., p. 647) suffered compression when exhausted of air; the air buoyancy was thus unknowingly diminished, and the apparent weight of hydrogen thereby reduced below its true value. The shrinkage was determined by weighing the globe under water after it had been nearly filled with water and then exhausted at the pump, and again after its vacuous space had been filled with air. The contraction due to exhaustion amounted to about 1.6 c.c., and the consequent average correction to be added to the amount of hydrogen is 0.00198 gram, whence the corrected atomic

weight of oxygen = 15·869, and the composition of water is oxygen (Dumas) $88\cdot864 \pm 0\cdot0044$, and hydrogen (Cooke and Richards) $11\cdot193 \pm 0\cdot0011$, total 100·057. There is therefore in Dumas' or in the authors' method some constant source of error to account for the excess of 0·057 per cent. That the hydrogen was not perfectly burnt, as suggested by Rayleigh, seems, for several reasons given, improbable; the balance and weights were verified, and an allowance was made for the air dissolved in the water weighed.

The correction now made for the shrinkage of the glass balloon by decreased pressure has not before been made, and it obviously must be applied to all determinations of gas or vapour-densities hitherto made, and to all atomic weight determinations of any kind which involve the calculation of the weight of a measured volume of any gas or vapour; except, however, in the case of hydrogen the correction will be inconsiderable.

H. B.

Potassium Hypiodite. By C. M. VAN DEVENTER and H. L. VAN'T HOFF (*Chem. Centr.*, 1888, 362—363, from *Maandbl. Naturwetensch.*, 14, 98).—That potassium hypiodite is contained in a solution of iodine in potassium hydroxide, provided the solution is made in the cold, is shown by the fact that it behaves quite differently to one which has been heated and then allowed to cool. When to a cold solution of iodine in potash, alcohol is added, iodoform is formed in large quantity, whilst in a cold solution, which has previously been heated, the brown colour has disappeared, and alcohol does not generate any iodoform. Another proof is contained in the fact that a far greater quantity of iodoform is formed when iodine is added to a solution of potassium hydroxide in alcohol than when alcohol is added to a solution of iodine in potassium hydroxide. In the latter case, the hypiodite is partly converted into iodate, whilst in the former the potassium hypiodite can react with the alcohol when first it is formed.

J. W. L.

Colloidal State of Sulphides. By C. WINSSINGER (*Bull. Soc. Chim.*, 49, 452—457).—By employing one of the following methods, all the sulphides which were examined, except manganese sulphide, were obtained in the colloidal state. (Compare Spring and de Bock, this vol., pp. 227, 228). (1.) The precipitated sulphide is washed by decantation with pure cold water or a dilute solution of hydrogen sulphide; as the impurities are removed, the sulphide gradually becomes soluble and finally dissolves completely. (2.) The sulphide is formed in a solution so dilute that all extraneous compounds can be removed by dialysis before the sulphide becomes insoluble. (3.) The sulphide is formed in a liquid without the introduction of any substance capable of causing coagulation.

Mercuric sulphide, prepared by precipitating a dilute solution of a mercuric salt with hydrogen sulphide, was treated by the first method. The concentrated solution thus obtained is black and opaque, but a dilute solution is brown with a slightly greenish tint by reflected light. A sufficiently dilute solution can be boiled until the whole of the hydrogen sulphide is expelled, or it can be kept for more than a month, without undergoing any alteration. Colloidal zinc sulphide

is easily obtained by the first method, or by passing hydrogen sulphide through water containing pure zinc hydroxide in suspension. The solution is slightly opalescent, and can be boiled until the whole of the hydrogen sulphide is expelled without undergoing change; when boiled for a longer time the sulphide is precipitated, but, after cooling, it is readily redissolved when a stream of hydrogen sulphide is passed through the solution. A dark-brown solution of tungsten trisulphide is obtained when a little more dilute hydrochloric acid than is necessary to saturate the alkali is added to a solution of sodium thiotungstate. The solution can be filtered through paper.

A solution of molybdenum sulphide, prepared by adding an excess of dilute acetic acid to a solution of potassium thiomolybdate and dialysing, coagulates when filtered through paper. Colloidal indium sulphide is obtained when a stream of hydrogen sulphide is passed through an aqueous solution of the hydroxide; the dark golden-yellow solution can be freed from hydrogen sulphide by boiling, but it is coagulated by acetic acid or salts.

The sulphides of thallium, lead, bismuth, platinum, gold, palladium, and silver were prepared in the colloidal state by the second method; they all form reddish-brown solutions. Solutions of the sulphides of gold and silver can be kept for more than two months without change. Very dilute solutions of the sulphides of iron, nickel and cobalt were obtained by the second method; they are greenish-brown, oxidise very readily, and are very prone to coagulation.

All the solutions, with the exception of that of zinc, give very similar absorption-spectra; a dark band extends from the extremity of the violet to the green, where it gradually disappears; the extreme end of the red is faintly obscured, and the whole visible spectrum is only very slightly luminous. The spectra of the sulphides of indium and cadmium (compare Prost, this vol., p. 653) can be readily distinguished; they are more luminous, and the dark band ceases more abruptly in the region of the green.

The facility with which the sulphide of an element can be obtained and retained in the colloidal state seems to be a function of the atomic weight of the element.

F. S. K.

Sodium Dithiopersulphate. By A. VILLIERS (*Compt. rend.*, **106**, 1354—1356).—In the preparation of this salt (this vol., p. 649) it is not necessary to cool the solution with ice. The crystals may be separated from admixed trithionate by exposing the mixture to air. The trithionate effloresces and the unaltered crystals of the dithiopersulphate are easily picked out. Tetrathionate is produced in addition to the other two salts, and it is possible that the reactions take place in accordance with the equations: $2\text{Na}_2\text{S}_2\text{O}_3 + 3\text{SO}_2 = \text{Na}_2\text{S}_4\text{O}_6 + \text{Na}_2\text{S}_3\text{O}_6$, and $2\text{Na}_2\text{S}_2\text{O}_3 + 8\text{SO}_2 = \text{Na}_2\text{S}_4\text{O}_6 + \text{Na}_2\text{S}_3\text{O}_6$.

Sodium dithiopersulphate crystallises in anhydrous, rhombic prisms with the faces *m* terminated by acute bevels formed by the faces *e*, the angles being *mm* $130^\circ 2'$; *e*₁*e*₁ $86^\circ 10'$; *e*₁*m* 108° . When the salt crystallises at a low temperature, it combines with 2 mols. H₂O. The anhydrous crystals do not alter when exposed to air, but melt at about 125° and intumesce at 140° , giving off sulphurous anhydride and

leaving a residue which contains a sulphate and free sulphur, but no alkaline sulphide. The hydrated salt decomposes slowly in the cold and rapidly when heated, with evolution of sulphurous anhydride and formation of the trithionate. Sulphurous anhydride has no action on the trithionate at the ordinary temperature.

The dithiopersulphate does not reduce potassium permanganate even when heated, but is converted into sulphate by the action of bromine, five equivalents of bromine being required for each equivalent of the salt, a result which confirms the formula ascribed to the salt. Its solution gives no precipitates with metallic salts except mercuric chloride, which produces a precipitate of sulphur. When boiled with cupric sulphate, there is no precipitate of cuprous sulphide as with the trithionate, except after prolonged ebullition; concentrated mineral acids seem to liberate dithiopersulphuric acid from its salts without decomposing it. Nitric acid above a certain strength, however, oxidises it rapidly, and even explosively, with precipitation of sulphur and evolution of nitrogen oxides.

The name dithiopersulphuric acid must be regarded as merely provisional. C. H. B.

Preparation of Nitrogen Tetroxide. By B. SETLICK (*Chem. Centr.*, 1888, 461, from *Listy Chem.*, 11, 241—242).—The technical application of liquid nitrogen tetroxide to the preparation of explosive substances led the author to determine the yield of tetroxide obtained by the usual methods of preparation. 60 to 70 per cent. of the theoretical yield was obtained by heating lead or calcium nitrate, and by reducing nitric acid with starch, &c. The author has also investigated the yield of nitrogen tetroxide on oxidising nitric oxide with pure oxygen and air. The nitrogen tetroxide when formed was led through two cooled receivers to condense the gas, and then through sulphuric acid to dissolve the remainder. With air, the yield was 138.6 grams (of which 18 grams condensed); with a mixture of equal parts of air and oxygen, 129.8 grams (of which 80.3 grams condensed) out of a theoretical yield of 156.8 grams. With oxygen alone, the yield was 92.8 grams (of which 74 condensed) out of a possible 102 grams. J. P. L.

Preparation of the Alkali Salts of Hydroxylaminedisulphonic Acid and of Hydroxylamine. By F. RASCHIG (*Chem. Zeit.*, 12, 219).—Alkaline hydroxylaminedisulphonates may be prepared by adding the alkaline hydrogen sulphite (2 mols.) in concentrated aqueous solution to the alkaline nitrite (1 mol.) at a temperature not exceeding 0° for the sodium salt or 40° for the potassium compound. They may also be prepared by passing sulphurous anhydride to excess into a solution containing the alkaline nitrite (2 mols.) and either the alkaline carbonate (1 mol.), or the hydroxide (2 mols.). The potassium salt may also be obtained by adding a soluble potassium salt to a solution of sodium hydroxylaminedisulphonate, in which case the potassium hydroxylaminedisulphonate settles out as a compact, crystalline mass. When solutions (which must not react alkaline) of these salts or of the hydroxylaminemonosulphonates are heated for

some time at 100°, or for a short time at 130°, they are resolved into hydroxylamine and alkaline sulphates, which may be readily separated by fractional crystallisation.

D. A. L.

Electrolysis of the Acids of Phosphorus. By G. JANEČEK (*Chem. Centr.*, 1888, 273—274, from *Rad jngoslavenske Akad.*; Agram, 83, 186—200).—The electrolysis of melted orthophosphoric acid at a temperature below that at which it becomes dehydrated, dehydrates it rapidly, hydrogen and oxygen being evolved at the electrodes. The dehydration proceeds first to the formation of pyrophosphoric acid, and later to that of metaphosphoric acid. The liberated oxygen contains a quantity of ozone. The metaphosphoric acid is further decomposed with formation of phosphorous acid, large quantities of spontaneously combustible phosphoretted hydrogen being evolved at the same time.

J. W. L.

Pyrophosphorous Acid. By L. AMAT (*Compt. rend.*, 106, 1400—1402).—When the salt $2\text{NaH}_2\text{PO}_3 + 5\text{H}_2\text{O}$ is heated at 160°, it loses 6 mols. H_2O , and yields the pyrophosphite $\text{Na}_2\text{H}_2\text{P}_2\text{O}_5$. The crystals should previously have been partially dehydrated in a vacuum. Sodium pyrophosphite is very soluble in water, and the solution gives no precipitate with silver nitrate, but metallic silver separates out very slowly in the cold, more rapidly on heating. Monosodium phosphite gives with silver nitrate an immediate white precipitate which rapidly becomes black. The pyrophosphite is neutral to methyl-orange and phenolphthaleïn, whilst the phosphite is neutral to methyl-orange but acid to the phthaleïn. A cold solution of the salt alters very slowly, but if heated, it is reconverted into the phosphite. If the boiling solution is gradually mixed with sodium hydroxide, disodium phosphite is obtained.

Only the monosodium salts of the monobasic acids, such as metaphosphoric and hypophosphoric, are neutral to phenolphthaleïn, and since the sodium salt of pyrophosphorous acid is neutral to the phthaleïn, it follows that this acid is also monobasic.

C. H. B.

Note by Abstractor.—The conclusion that pyrophosphorous acid is monobasic is only tenable on the old notation, $\text{O} = 8$. Adopting the modern notation, it must be at least bibasic.

C. H. B.

Arsenic Compounds. By K. PREIS (*Chem. Centr.*, 1888, 657, from *Listy Chem.*, 12, 141—148).—*Sodium Oxythioarsenates.*—The reaction between arsenic trioxide and a solution of sodium sulphide varies according to the respective masses employed. The compounds described below are formed by the interaction of 1 molecular proportion of arsenic trioxide with 2 of sodium sulphide. In the warm, a brown precipitate is produced; if the turbid solution is boiled for five minutes, filtered hot, and then allowed to cool, it is converted into a magma of colourless needles from which four oxythioarsenates, besides normal sodium arsenate, were obtained by fractional crystallisation: (1) $\text{Na}_3\text{AsSO}_3 + 12\text{H}_2\text{O}$; (2) $\text{Na}_2\text{HASO}_3 + 8\text{H}_2\text{O}$; (3) $\text{Na}_3\text{AsS}_2\text{O}_2 + 2\text{H}_2\text{O}$; (4) $\text{Na}_{12}\text{As}_4\text{S}_5\text{O}_{11} + 48\text{H}_2\text{O}$.

J. P. L.

Crystalline Silicic Acid. By H. HAGER (*Chem. Centr.*, 1888, 461, from *Pharm. Centralb.*, 29, 115).—To prepare this crystalline silicic acid, the author treats siliceous limestone with crude concentrated hydrochloric acid until carbonic anhydride ceases to be evolved, then filters and adds to the filtrate 29 to 31 per cent. hydrochloric acid until a cloudiness appears. After remaining 24 hours the solution is decanted, the precipitate strained and washed, finally with distilled water, then dried on porcelain. Silicic acid so obtained is crystalline and corresponds to the formula $\text{H}_2\text{SiO}_3 + 3\text{H}_2\text{O}$ or $\text{H}_2\text{SiO}_3 + 2\text{H}_2\text{O}$. It is more soluble than the amorphous variety, and probably preferable as an indifferent covering for wounds and for administering internally. J. P. L.

Alkaline Phosphites. By L. AMAT (*Compt. rend.*, 106, 1351—1354).—*Monosodium phosphite*, $2\text{NaH}_2\text{PO}_3 + 5\text{H}_2\text{O}$, is obtained by adding sodium hydroxide or carbonate to phosphorous acid until the solution is neutral to methyl-orange. The liquid is then concentrated by evaporation and the salt crystallises. Not unfrequently a supersaturated solution is obtained which crystallises in contact with a fragment of the solid phosphite. If no crystals of the phosphite are at hand, the solution is concentrated until it has the composition of the crystals and is cooled to a low temperature. The salt is recrystallised from water and dried by exposure to air. It can also be obtained by the action of phosphorus trichloride on sodium carbonate, but the separation of the sodium chloride is difficult.

Monosodium phosphite is very soluble in water and melts at 42° . At 100° the fused salt loses water and the liquid deposits crystals which may be either a lower hydrate or the anhydrous salt. If heated at 100° for a long time, it becomes completely dehydrated; it also becomes anhydrous in a dry vacuum. When heated above 130° the phosphite changes into sodium pyrophosphite.

Potassium phosphite is obtained in a similar manner. It forms anhydrous crystals, which are difficult to purify by recrystallisation.

C. H. B.

Sodium Trithionate. By A. VILLIERS (*Compt. rend.*, 106, 1356—1357).—Sodium trithionate, $\text{Na}_2\text{S}_3\text{O}_6 + 3\text{H}_2\text{O}$, crystallises in rhombic prisms with the faces *m* and *g* terminated by the domes e_1e_1 . The angles are as follows: *mm* $126^\circ 30'$; *mg* $116^\circ 40'$; e_1g_1 $124^\circ 50'$; e_1m $105^\circ 10'$; e_1e_1 $110^\circ 14'$.

C. H. B.

Extraction of Lead from Residues obtained in the Manufacture of Zinc. By E. PROST (*Bull. Soc. Chim.*, 49, 682—685).—The residues experimented on are obtained in the reduction of zinc and are called "lead-cinders;" they are separated mechanically into "fine cinders," containing 15 to 20 or even 22 per cent. of lead, and "granulated metal" containing at the most 10 per cent. of lead. The richer samples contain as much as 400 grams of silver per tonne and the "granulated metal" 225 grams per tonne. The following analyses show the average composition of these residues:—

Fine Cinders.

	(1).	(2).
Pb	18.25	17.22
SiO ₂	15.52	16.00
Fe	36.50	38.10
Zn	6.14	5.00
CaO	5.40	6.15
Carbon (approx.)	3.00	3.00
Ag per tonne	340.0 grams	340.0 grams.

When the "fine cinders" are placed in a crucible, covered with a layer of powdered coal and heated in a wind-furnace, the whole of the lead excepting the portion which volatilises is obtained in the metallic state. A mixture of equal parts of "fine cinder" and "granulated metal," containing 12.57 per cent. of lead, gives a readily fusible slag, the composition of which is SiO₂ 50.85 per cent., Al₂O₃ 5.10 per cent., FeO 20.14 per cent., and CaO 23.54 per cent. A similar mixture containing 13.06 per cent. of lead is more refractory, but when heated in very thin layers (of about 2 cm. thickness) fusion is complete, and about 84 per cent. of the lead is recovered. The composition of this slag is SiO₂ 50.84 per cent., FeO 17.09 per cent., Al₂O₃ 11.54 per cent., CaO 19.96 per cent. Fusion takes place most rapidly when the silica, lime, and alumina are in the proportion shown by the first analysis.

The lead contains almost the whole of the silver; in cases where the yield of lead attained 84 per cent., it contained 92 per cent. of the silver present in the original mixture. F. S. K.

New Halogen Compounds of Lead. By R. G. GRISSON and B. THORP (*Amer. Chem. J.*, 10, 229—232).—Lead chlorothiocyante, PbCl₂.Pb(CNS)₂, is obtained by digesting the chloride with potassium thiocyanate and then recrystallising from boiling water. Ammonia converts it very slowly into lead hydroxide, and neither of the acid radicles is removed before the other. Lead bromothiocyante, PbBr₂.Pb(CNS)₂, similarly produced, forms slightly brownish crystals, the salt, 8PbBr₂.Pb(CNS)₂, is obtained by acidifying with hydrobromic acid. Lead iodothiocyante, PbI₂.3Pb(CNS)₂, is formed with some little difficulty.

Lead chlorocyanide, PbCl₂.2Pb(CN)₂, is formed by digesting lead chloride with potassium cyanide; it is quite insoluble in water, and decomposes on keeping. No double salts of the ferrocyanide could be obtained.

Lead Bromiodide.—By crystallising a solution of lead iodide in hydrobromic acid, the following substances were obtained: PbBr₂.PbI₂; 3PbBr₂.PbI₂; 6PbBr₂.PbI₂; and lastly lead bromide. Lead chlorobromiodide was prepared by crystallising a solution of all three salts: the crystals contain uniformly 61.5 per cent. of lead. H. B.

Relation of the Atomic Weights of Copper and Silver. By T. W. RICHARDS (*Amer. Chem. J.*, 10, 182—187).—The results recently obtained by W. N. Shaw (*Abstr.*, 1887, 444) by the electrolytic method, are higher than those previously obtained for the atomic

weight of copper, with the exception of the determinations of Dumas; namely, Berzelius, 63.153 ($O = 15.963$); Erdmann and Marchand, 63.316; Millon and Commaille 62.979; Dumas (sulphide as well as oxide), 63.5; Hampe, 63.197 and 63.173; Shaw, 63.33 or 63.36. The present results were obtained by a method tried and discarded by Hampe, namely, the precipitation of silver nitrate by metallic copper. The precipitation, however, must be effected at -1° , and the solution of silver nitrate should be tolerably strong (5 to 20 per cent.). Under these conditions, the precipitated silver is very easily manipulated and is quite free from copper, whilst at higher temperatures, the action is more rapid, but gases are evolved and the silver precipitate contains copper compounds. The number $Cu = 63.437$ ($Ag = 107.675$), is obtained as the mean of six very concordant determinations, the greatest difference between the estimations being 0.020 and the probable error ± 0.0023 . This number agrees nearly with that obtained by Dumas with the sulphide of copper. The method is proposed as a means of preparing chemically pure silver.

H. B.

Atomic Weight of Copper. By T. W. RICHARDS (*Amer. Chem. J.*, 10, 187—191).—After the completion of the previous experiments it was found that a temperature of 150° , at which this silver was dried, was not sufficient to drive off all moisture; in the only case in which this error was examined the correction amounted to $+0.015$. The secondary reaction, occurring at temperatures above 0° and which causes the precipitation of green basic copper nitrate, is written $4AgNO_3 + 4Cu + 3H_2O = Cu(NO_3)_2, 3Cu(OH)_2 + 2Ag_2 + NO + NO_2$. The copper of which two samples were taken (Lake Superior and German, which universally contain comparatively large amounts of arsenic) was purified much as before. The average results obtained were respectively 63.449 with a probable error of ± 0.0010 , and 63.450 with a probable error of ± 0.0013 , whilst the average result obtained from the weight of the precipitate dried at 150° is 63.436. The agreement of results points to the purity of the materials, and it is believed to the absence of any constant error. It was found impracticable to use sulphate of silver in place of the nitrate.

H. B.

Formation of Crystallised Ferric Hydroxides in the Dry Way. By G. ROUSSEAU and J. BERNHEIM (*Compt. rend.*, 106, 1530—1532).—2 grams of precipitated ferric hydroxide dried at 100° is added to 15 grams of fused sodium hydroxide in a platinum crucible, and the mixture is heated at the highest temperature of the bunsen flame for about an hour and a half, care being taken that all the sodium hydroxide is not volatilised. The interior of the cooled crucible is covered with lustrous needles and lamellæ of the composition $20Fe_2O_3, 32H_2O, 3Na_2O$. They dissolve readily in acids, and begin to lose water at 120° . At 150° , 9.54 per cent. of water is given off, at $250-300^\circ$, 3.7 per cent., and the remainder at dull redness. The dehydrated substance resembles specular hæmatite in appearance, and its constitution seems to have been profoundly altered. It is attacked with difficulty by acids, but imparts an alkaline reaction to water. This latter fact indicates that the com-

pound has dissociated, and that the presence of water is essential to the stability of the complex molecule. Mallard has shown that ferric oxide is monobasic, and will not accumulate in a saline molecule in the same manner as silica, titanium oxide, &c. It may be assumed, therefore, that in the product described, sodium oxide has replaced water, molecule for molecule. At higher temperatures the compound loses water and sodium oxide and is converted into compounds corresponding with the lower hydrates.

When ferric hydroxide is fused with sodium hydroxide at about 110° violet-red lamellæ are formed, which contain Fe_2O_3 88.7, Na_2O 2.47, H_2O 8.61 per cent. If it is assumed that the sodium oxide has replaced water, this product corresponds with goethite, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. It loses 3.65 per cent. at 150° , 3.33 at 300° , and the remainder at a red heat.

If 2 grams of dried ferric hydroxide is heated to bright redness for half an hour with 6 grams of sodium carbonate, and the product is mixed with excess of sodium chloride and heated at an orange-red heat until the greater part of the sodium chloride is volatilised, black crystals and lustrous black plates are obtained which have the composition Fe_2O_3 83.97, Na_2O 2.81, H_2O 12.39 per cent. Assuming the soda to have replaced water, these numbers correspond with $5\text{Fe}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$.

If ferrous sulphate and sodium chloride are heated to redness for one hour and the product poured on a metal plate and extracted with water, crystalline plates are obtained of the composition Fe_2O_3 94.30, Na_2O 0.78, H_2O 4.09 per cent., which corresponds with turgite, $2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. This product is less soluble in acids than those previously described; it loses 0.92 per cent. at 150° , 1.23 per cent. at 300° , and the remainder at a red heat. The residue has an alkaline reaction.

All these compounds contain sodium oxide and water in the proportion of 1 mol. of the former to 10 mols. of the latter, a fact which favours the supposition that the first compound is gradually dissociated, the sodium oxide and water being eliminated simultaneously in these proportions.

No similar results were obtained with potassium hydroxide.

C. H. B.

Uranates of Ammonium and of certain Amines. By A. J. CARSON and T. H. NORTON (*Amer. Chem. J.*, **10**, 219—221).—The analyses of normal uranates of the metallic bases always show considerable differences between the practical and theoretical percentages of uranium. The same is now shown to hold for the uranates of ammonium, methyl-, dimethyl-, trimethyl-, ethyl-, diethyl-, triethyl-, and isobutyl-, and phenyl-ammonium. The only salt that at all agreed with the theory was the ethylammonium salt.

H. B.

Influence of Hydrochloric Acid on the Solubility of Stannous Chloride. By ENGEL (*Compt. rend.*, **106**, 1398—1400).—The addition of hydrochloric acid to a solution of stannous chloride at first precipitates a molecule of the salt for each molecule of acid added, a result which agrees with the author's general law. As the

proportion of hydrochloric acid increases, the precipitation of the salt gradually ceases. The solubility of the stannous chloride, then, increases with the amount of acid added, but when a certain proportion is reached it remains constant.

If dry hydrogen chloride is passed over hydrated stannous chloride, $\text{SnCl}_2 + 2\text{H}_2\text{O}$, a liquid is formed which contains 19.6 per cent. of water; sp. gr. 2.193. Crystals of the hydrate, $\text{SnCl}_2 + \text{H}_2\text{O}$, are formed at the same time. The liquid product has a composition which agrees fairly well with the formula $\text{SnCl}_2 \cdot \text{HCl} + 3\text{H}_2\text{O}$. It does not crystallise at -21° , but at -40° ; it deposits slender, silky needles which melt at -28° . Portions of the liquid removed at different stages of the crystallisation have the same composition as the original liquid, and it follows that the crystals are a hydrochloride of stannous chloride of the composition $\text{SnCl}_2 \cdot \text{HCl} + 3\text{H}_2\text{O}$.

C. H. B.

Action of Chlorine on Gold. By L. LINDET (*Bull. Soc. Chim.*, 49, 450—451).—Auric chloride is formed when gold sponge is treated with chlorine at any temperature, but the product always contains a considerable proportion of unattacked metal, and, when the temperature is above 175° , aurous chloride is also present (compare Krüss and Schmidt, this vol., p. 28). The quantity of auric chloride formed increases with the temperature, but the proportion of aurous chloride increases equally.

F. S. K.

Rhodium Sesquisulphide. By E. LEIDIE (*Compt. rend.*, 106, 1533—1536).—The only method which yields pure rhodium sesquisulphide, Rh_2S_3 , is to heat the chloride, Rh_2Cl_6 , prepared at 440° , in a current of pure and dry hydrogen sulphide at 360° . It forms blackish, crystalline plates which retain the form of the chloride. At a dull red heat in an atmosphere of nitrogen, it loses 8 per cent. of sulphur, and the residue corresponds with Berzelius's supposed monosulphide. If heated at bright redness in a vacuum or in a brasqued crucible it yields a regulus which has a metallic appearance but contains 9 per cent. of sulphur. The whole of the sulphur can only be expelled in the oxyhydrogen flame. Rhodium sesquisulphide is insoluble in alkalis and is not attacked by bromine-water nor by hydrochloric acid, nitric acid or aqua regia.

Hydrated rhodium sulphide obtained by the ordinary methods and dried contains more sulphur than corresponds with the sesquisulphide. When heated at 440° in a vacuum, it loses sulphurous anhydride and water, and the residue approximates closely in composition to the sesquisulphide. If a solution of a rhodium salt is mixed with a large excess of hydrogen sulphide in a closed vessel, precipitation of the rhodium is complete in a few minutes at 100° but requires months at the ordinary temperature. In both cases the product is a brownish-black precipitate of the hydrosulphide, $\text{Rh}_2\text{S}_3 \cdot 3\text{H}_2\text{S}$, which is insoluble in alkalis and in hydrochloric or nitric acid, but is attacked by bromine-water and aqua regia. When heated with 500 times its weight of water in a closed vessel or in an atmosphere of nitrogen, the hydrosulphide is decomposed into rhodium sulphide and hydrogen sulphide. Whenever a rhodium salt

is precipitated by hydrogen sulphide at 100° , the hydrosulphide is formed, but it immediately decomposes, the change taking place more readily in presence of an excess of rhodium salt than in presence of water alone.

If a normal salt of rhodium, such as an alkaline rhodiochloride, is treated with an excess of a concentrated solution of an alkaline monosulphide, a compound of rhodium sulphide with the alkaline sulphide is precipitated, and is stable in presence of excess of the latter, but is decomposed by water. When the liquid contains not more than 16 mols. of water to each molecule of sodium sulphide the precipitate has the composition $\text{Rh}_2\text{S}_3, 3\text{Na}_2\text{S}$; with at least 110 mols. of water, the precipitate is rhodium sulphide alone, and between these limits the double sulphide is gradually dissociated as the proportion of water increases. With 550 mols. of water to each molecule of sodium sulphide, the precipitate formed in the cold is yellow rhodium hydroxide, the alkaline sulphide being completely dissociated by the water into the hydroxide and hydrogen sulphide.

Potassium sulphide gives precisely similar results. C. H. B.

Rutheniates and Per-rutheniates. By H. DEBRAY and A. JOLY (*Compt. rend.*, **106**, 1494—1500).—60 grams of potassium hydroxide is dissolved in 250 grams of water, heated to 60° , and gradually mixed with 50 grams of ruthenium peroxide fused under water. Oxygen is evolved and the liquid first becomes green and then almost black. When the change is complete the liquid is allowed to cool in a closed vessel. It then deposits small crystals which are at once dried on porcelain and afterwards in a dry vacuum. When dry it does not alter on exposure to air.

Potassium per-rutheniate, KRuO_4 , obtained in this manner, forms opaque, black, highly lustrous, quadratic octahedra, the dominant face being a' , but $b\frac{1}{2}$ is also present; plane of cleavage a' ;

$$h : b :: 1.15543 : 1.$$

In composition it is identical with the crystals obtained by the action of chlorine on the rutheniates. At 400° in a vacuum the per-rutheniate rapidly decomposes with evolution of oxygen and formation of the rutheniate and ruthenium dioxide, or possibly a compound of potassium oxide with a lower oxide of ruthenium. Dry chlorine decomposes the per-rutheniate in the cold with formation of potassium chloride and ruthenium peroxide.

Potassium rutheniate, K_2RuO_4 , is obtained by evaporating the mother-liquor from the per-rutheniate in a dry vacuum, and also directly by adding 50 grams of the peroxide to a larger proportion of alkali (70 grams) and water (500 grams) than in the preparation of the per-rutheniate, care being taken that the temperature of the liquid does not exceed 60° . It forms rhombic prisms with the faces $m, h', g^3, p, a',$ and a^4 ; $a : b : c = 0.7935 : 1 : 1.1973$. Measurements of the angles are given. The crystals alter rapidly on exposure to air, and even after being dried absorb moisture and carbonic anhydride. They contain 1 mol. H_2O , which is not given off at 106° in a vacuum. At 200° they become anhydrous without being reduced,

and the anhydrous salt does not alter in a vacuum at 440° . The rutheniate is very soluble in water, forming a very deep-orange solution, which, when diluted or mixed with acids, changes, in a manner similar to potassium manganate, into the per-rutheniate and the pentoxide, thus: $4\text{K}_2\text{RuO}_4 + 3\text{H}_2\text{O} = 2\text{KRuO}_4 + \text{Ru}_2\text{O}_5 + 6\text{KHO}$. With carbonic anhydride or chlorine, concentrated solutions yield a precipitate of the per-rutheniate, which decomposes into the pentoxide or the peroxide. Concentrated hydrochloric acid precipitates a mixture of the per-rutheniate and the pentoxide, but the precipitate redissolves with evolution of chlorine and formation of the sesquichloride.

When a solution of potassium per-rutheniate is mixed with an excess of the hydroxide it is converted into the rutheniate with evolution of oxygen. The decompositions of the rutheniate and per-rutheniate can be traced by the changes in colour.

Sodium per-rutheniate is obtained in a similar manner to the potassium salt, and crystallises with 2 mols. H_2O . The rutheniate does not crystallise well, and cannot readily be purified.

Barium hydroxide solution dissolves ruthenium peroxide with evolution of oxygen and formation of a black precipitate which rapidly changes into a vermilion-red, crystalline precipitate of *barium rutheniate*, $\text{BaRuO}_4 + \text{H}_2\text{O}$. The same compound is obtained by adding barium chloride to a solution of potassium rutheniate, and the strontium salt is formed as a brilliant, red precipitate in a similar manner. The calcium and magnesium salts are black.

Silver rutheniate is obtained as a very dense, black precipitate when silver nitrate is added to a solution of an alkaline rutheniate. The precipitation of the ruthenium is complete.

The per-rutheniates of the alkaline earths and the heavy metals have only a momentary existence. If barium chloride or silver nitrate is added to a solution of an alkaline per-rutheniate a precipitate of the corresponding rutheniate is formed, and the liquid has a yellow colour and contains per-ruthenic acid.

Although in their relations and decompositions ruthenic and per-ruthenic acids are analogous to manganic and permanganic acids, the ruthenates and per-ruthenates are not isomorphous with the manganates and permanganates respectively, and do not crystallise with the same quantities of water of crystallisation. C. H. B.

Atomic Weight of Osmium. By K. SEUBERT (*Ber.*, 21, 1839—1847).—The atomic weight of osmium was found to be 191.12 as the mean of several analyses of two different samples of ammonium osmiochloride and potassium osmiochloride. In the author's opinion this result is rather too high, and the true atomic weight is more probably 190.8. Osmium therefore falls into its right place below iridium in the natural system.

The ammonium osmiochloride, $(\text{NH}_4)_2\text{OsCl}_6$, was obtained by adding a solution of ammonium chloride to an alcoholic solution of osmium chloride; the precipitate is washed with ice-cold water until free from excess of ammonium chloride, dissolved in water at about 50° , and filtered. When the solution is evaporated in a partial vacuum, well-defined octohedra are deposited which appear dark red in the

liquid but black when dry. The powdered substance is bright red.

Potassium osmiochloride, K_2OsCl_6 , was prepared by heating the metal, obtained from the ammonium salt, with potassium chloride in a stream of chlorine, washing the product with ice-cold water until free from excess of potassium chloride, and recrystallising from luke-warm water. It is more stable in solution than the ammonium salt, to which, however, in the dry state it is very similar.

The second sample of potassium osmiochloride was prepared in like manner from a different specimen of osmium. The second sample of ammonium osmiochloride was obtained by reducing the potassium osmiochloride just mentioned in a stream of hydrogen, washing the residue until free from potassium chloride, and heating it with pure sodium chloride in a stream of chlorine. The concentrated, filtered solution of the resulting sodium osmiochloride was precipitated with a saturated solution of ammonium chloride, the precipitate washed consecutively with dilute ammonium chloride solution and ice-cold water and recrystallised from water.

The method of analysis was practically the same as that described in the case of platinum (Abstr., 1881, 514), but in weighing the finely divided osmium care must be taken on account of the readiness with which it oxidises, a fact which makes the results of doubtful trustworthiness.

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F. S. K.

Mineralogical Chemistry.

Minerals from New Localities in Bohemia. By F. KATZER (*Chem. Centr.*, 1888, 493, from *Tschermak's Mitth.*, 9, 404—415).—*Bornite* (purple copper ore) from Woderad. Hardness above 3. Sp. gr. 4·91. Its composition is—

S.	Cu.	Fe.	Insol.	Total.
23·76	59·85	15·62	1·23 =	100·46

and corresponds to the formula $3\text{Cu}_2\text{S}, \text{CuS}, 2\text{FeS}$.

Rutile from Sobeslau. Rutile is of general occurrence in Bohemia, especially in the neighbourhood of the Bohemian forest gneiss and the Bohemian-Moravian primitive rocks, and also in the alluvial deposits formed by the weathering of these formations. It occurs abundantly in the alluvial clay and sand at the above-named places partly in clearly defined crystals; its hardness is above 6. Sp. gr. 4·35.

Calcite from Sobeslau. In the clay from the subsoil of miocene sand an extraordinary fossil was found resembling petrified wood, but which owed its peculiar structure to a radiated arrangement of the calcite. It much resembles arragonite, but the mean of four determinations of the sp. gr. was 2·67. Its composition is—

CaO.	CO ₂ .	Fe ₂ O ₃ .	H ₂ O.	Insol.	Total.
53·12	42·63	1·98	0·23	0·19	98·15

Orthoclase from Babitz. The porphyritic granite of the mid-Bohemian granite formation changes after contact with the schists, to a strikingly coarse-grained orthoclase; especially abundant and weathered on the surface at the above-mentioned place. Two varieties can be distinguished by their colour and durability:—a red variety which weathers slowly, and a whitish variety which undergoes change much more readily. An analysis of the latter variety gave—

SiO ₂ .	Al ₂ O ₃ with Fe ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	Loss on heating.
63·86	19·42	0·48	12·89	2·06	0·68

Tourmalin from Straschin, Mnichowitz, Sobeslau, Kuhrau. It is widely diffused throughout the primitive rocks. Nevertheless, it is more abundant and more constant in its occurrence where the granite is in contact with the schist. The black crystals from Straschin, measuring as much as 6 cm. long, are often broken off short and cemented by felspar. The tourmalin of Kuhrau occurs in crystals as much as 10 cm. long and 2 cm. thick, often broken and in combination with red orthoclase and potash mica. J. P. L.

Halotrichite from the Tyrol. By J. HOCKAUF (*Jahrb. f. Min.*, 1888, ii, Ref., 58, from *Verh. geol. Reichsanst.*, 1887, 152—154).—The author has analysed the crusts of a white, yellow, or red colour, which occur as efflorescence on the pyrites-bearing micaceous clay-slate of the Vilmösthäl. The specific gravity of the material was 1·98. Analysis gave the following results:—

SO ₃ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	K ₂ O.	H ₂ O.	Total.
32·97	15·05	6·66	1·77	0·62	0·47	0·10	0·38	41·98	100·00

Of the proportion of water, 27—29 per cent. was given off at 100°, and the remainder at 320—350°. The mineral closely resembles the halotrichite of Idria. B. H. B.

Mineralogical Notes. By A. FRENZEL (*Chem. Centr.*, 1888, 492, from *Tschermak's Mitth.*, 9, 397—400).—In a sample of copiapite, from Valparaiso, a new iron sulphate was found, to which the name *Hohmannite* has been given. It consists of broad-leaved, radial-stemmed aggregates, of a lustrous, chestnut-brown colour. It contains (1)—

	Fe ₂ O ₃ .	SO ₃ .	H ₂ O.
(1.)	40·05	33·88	29·63
(2.)	37·26	35·58	27·62

and corresponds with the formula $2\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 + 13\text{H}_2\text{O}$; hardness = 3; sp. gr. = 2·24; streak, yellow ochre colour. When exposed to the air it soon changes into a soft, yellow-ochre-coloured mass, which is insoluble in water, but soluble in weak hydrochloric acid. When dried over calcium chloride, it loses part of its water.

In the same copiapite a second iron sulphate was found, to which the author has given the name *amurantite*. It occurs in very minute

crystals, of a yellowish-red colour. Its composition is given in analysis (2) above; it corresponds with the formula $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 + 7\text{H}_2\text{O}$; citron-yellow streak. Sp. gr. 2.11.

Minerals occurring in Ehrenfriedersdorf:—Achroite, colourless tourmalin of the usual form, anatase new to Ehrenfriedersdorf, anglesite, apatite, arsenical pyrites, baryta, chlorite, fluorite, scheelite, wolframite, and tin ore. J. P. L.

New Analysis of Hohmannite. By A. FRENZEL (*Chem. Centr.*, 1888, 493, from *Tschermak's Mitth.*, 9, 401—403).—This analysis shows that hohmannite and amarantite have the same composition—

SO_3 .	Fe_2O_3 .	H_2O .
33.84	35.58	30.08

and, as Wülfing has shown, almost the same crystallographic and optical properties. Their difference on heating, nevertheless, provisionally prevents their being regarded as identical. J. P. L.

Analyses of Zeolites. By C. HERSH (*Jahrb. f. Min.*, 1888, ii, Ref., 1—5, from *Inaug. Diss.*, Zürich, 1887).—The author has made a series of careful analyses of zeolites. The results are as follows:—

	1.	2.	3.	4.	5.	6.	7.
SiO_2	46.12	46.12	47.36	49.28	43.84	45.72	53.58
Al_2O_3	26.25	28.22	20.13	18.52	20.99	16.79	24.07
CaO	14.37	—	8.09	9.36	5.89	—	0.85
BaO	—	—	—	trace	—	22.34	—
Na_2O	—	15.87	1.99	0.72	5.78	—	13.60
K_2O	—	—	—	—	1.83	—	—
H_2O	13.89	9.91	22.54	22.02	21.97	15.18	8.29
Total	100.63	100.12	100.11	99.90	100.30	100.03*	100.39
Sp. gr.....	2.25	2.28	2.06	2.08	—	2.35	2.31

	8.	9.	10.	11.	12.	13.
SiO_2	58.18	56.91	41.56	39.87	52.24	43.23
Al_2O_3 ..	16.35	15.59	28.23	29.40	25.03	23.41
CaO	7.21	7.47	11.39	8.15	—	27.41
Fe_2O_3	—	—	—	—	—	1.68
Na_2O	2.07	1.14	4.20	8.26	—	—
K	—	—	—	—	4.05	—
F	—	—	—	—	2.21	—
H_2O	16.34	18.73	14.98	14.52	16.61	4.42
Total	100.15	99.84	100.36	100.20	100.14	100.15
Sp. gr.....	2.21	2.15	2.25	2.19	2.36	2.91

* 99.93 in original.

1. Scolezite, from Bulandstindr, in Iceland. 2. Natrolite, from Jakuben, in Bohemia. 3. Chabazite, from the Farøe Islands. In dry air this mineral lost 4·87 per cent. of water, and remained constant for a week; in moist air it took it up again. 4. Chabazite, from Oberstein, in the Nahethal. 5. Phacolite, from Richmond, in Victoria. 6. Har-motome, from St. Andreasberg, in the Harz. 7. Analcime, from the Cyclop Islands, near Catania, Sicily. 8. Stilbite, from Djupivogur, in Iceland. 9. Desmine, from Helgustadir, in Iceland. 10. Thomsonite, from Nalsøe, Farøe Islands. 11. Mesolite, from Hauenstein, in Bohemia. 12. Apophyllite, from Bergenhill, in New Jersey. 13. Prehnite, from Harzburg, in the Harz. B. H. B.

Proportion of Carbon and Hydrogen in Carbonaceous Schists: Contribution to the Study of the Formation of Coal. By W. SPRING (*Bull. Soc. Chim.*, 49, 11—16).—From analyses of carbonaceous schist taken from the region of the roof and wall of a bed of coal, at St. Gilles, Liège, it was found that the quantity of silica, alumina, and ferric oxide was practically the same in all samples, but the quantity of carbon and hydrogen varied very considerably. Samples from the roof contained about seven times as much carbon as those from the wall, and in both cases the quantity of carbon diminished as the distance from the bed increased. The quantity of hydrogen found by combustion was very high, owing to the fact that the substance does not give up the whole of its water at 120°; when, however, the water is entirely eliminated, the proportion of carbon to hydrogen was found to be the same in samples from the wall as in the coal itself, from which the conclusion may be drawn that the wall contains particles of coal only slightly altered. In samples from the roof, the proportion of carbon to hydrogen increases as the distance from the coal-bed increases. F. S. K.

Analysis of Lockport Sandstone. By H. W. WELD (*Amer. Chem. J.*, 10, 224).—The samples of "Medina" sandstone, from Lockport, N.Y., U.S., is characterised by the very high percentage of silica and the small amount of cementing material. It contains—

SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	CaO.	
96·41	0·70	1·65	1·02	H. B.

Nepheline-syenite from the Transvaal. By E. A. WÜLFING (*Jahrb. f. Min.*, 1888, ii, Mem., 16—34).—This rock occurs at the Zwart-Koppies, in the central Transvaal. It is of a light colour, and has a distinct porphyritic structure. Its primary constituents are orthoclase, plagioclase, augite, nepheline, sodalite, and, in smaller quantities, hornblende, mica, titanite, and opaque ores. The secondary products are hydrated ferric oxide and zeolites. The rock is thus a typical sodalite-bearing nepheline-syenite of porphyritic structure. Analysis gave the following results:—

	TiO ₂ .	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.
I.	0·00	43·69	28·64	1·40	—	0·20	2·88	trace
II.	0·26	60·57	13·00	10·15		0·44	2·57	0·60
III.	0·09	53·73	20·35	3·74	2·13	0·51	2·72	0·47
	K ₂ O.	Na ₂ O.	H ₂ O.	Cl.	Total.			
I.	3·88	15·17	4·25	0·59	100·70			
II.	7·45	3·31	0·59	—	98·94			
III.	6·05	7·94	2·02	0·23	99·98			

I. Analysis of the portion (39·03 per cent.) soluble in hydrochloric acid. II. Analysis of the insoluble portion. III. Complete analysis. The soluble portion appears to be a mixture of 30 per cent. of zeolite, 59 per cent. of nepheline, and 11 per cent. of sodalite. The Transvaal nepheline-syenite belongs to the group of rocks in which pyroxene is the predominating basic constituent. It is of special interest from the fact that it contains two augites, physically and chemically different, and that both contain alkalis.

B. H. B.

Petrography of the South-western Frontier between Minas and S. Paolo. By J. MACHADO (*Chem. Centr.* 1888, 496—497, from *Tschermak's Mitth.*, 9, 313, 360).—The rocks described from the abovementioned district belong to gneiss, different nepheline-syenites, a quartz-augite-diorite, and olivine diabase. The most important are the two first-named groups of rocks, and chief of all the gneisses, because they, by their whole habit, prove themselves to be the real members of the ancient formation. They consist of orthoclase, microcline, micropertite, plagioclase, biotite, quartz, more or less rich hornblende, and the accessory microscopic components, zircon, apatite, and magnetite, and they approximate in their structure sometimes to granite gneisses, and sometimes to augite gneisses. The nepheline-syenites which have been described from other parts of Brazil by Lasaulx and Rosenbusch, compose, according to previous researches, the Plateau of Pocos de Caldas. They are defined outwardly from the adjoining gneiss district by a striking infertility. The partly coarse and partly fine-grained light-grey rocks are composed chiefly of macroscopic orthoclase, nepheline, and augite. The ready decomposition of nepheline gives rise to a generally diffused transformation into a colourless and fibrous substance, with strong double refraction, in which cancrinite is supposed to exist. The green strongly pleochroite augite, which occurs in columns of irregular contour, in radially radiated and fibroglobular aggregates, belongs apparently throughout to the Aegirins.

Titanite occurs frequently; sodalite is locally plentiful, and similar in its habit to ditro; melanite scarce; and lastly, biotite occurs in varying quantities, but only as an accessory. A powdered and broken piece of nepheline-syenite found at Barreiro permitted the isolation of both augite and nepheline. Analyses 1 and 2 respectively :—

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.
(1.)	51·60	1·92	26·29	4·20	4·25	1·15	1·05	8·89	0·56
(2.)	48·63	25·11	2·58	—	3·52	1·15	1·47	7·50	11·66

The occurrence of modifications which sharply define themselves by a finer grained structure than usual, but which do not differ with regard to their mineral constituents, is noteworthy. The chemical composition of the latter is given in analysis (3). The fine-grained nepheline-syenites appear also, forming massive veins and rocks, similar in outward appearance to compact diorite, and even phonolites, and often coloured completely black, on account of their richness in augite. Wollastonite is sometimes met with in irregular masses, which appear to be as it were eaten away, or in sharply defined crystals, the presence of which was proved optically and chemically by the composition of the hydrochloric acid extract, which is given under analysis (4).

Orthoclase is the chief constituent of these fine-grained syenites, occurring for the most part in opaque twin crystals, according to the Carlsbad law. Next in importance comes nepheline, the amount of which (49·84 per cent.) is shown by the hydrochloric acid extract, and the composition of which is given under analysis (5). Analysis (6) shows the composition of the insoluble residue, which consists chiefly of potash felspar. Analysis (7) is the complete analysis of another fine-grained variety of syenite, in which lavinite was supposed to exist.

Finally, these interesting rocks are represented by perfectly compact and porphyritic gradations, which resemble phonolites much more than the fine-grained varieties, on account of their flat, conchoidal fracture, and their tendency to foliation. They are distinguished on the one hand by the presence of a vitreous base, and on the other hand by a frequently beautiful dendritic, or feather-formed aggregation of their augite.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MgO.	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Totals.
3	52·75	—	22·65	3·65	0·15	1·85	8·10	7·05	3·60	99·70
4	48·21	—	28·89	1·86	0·46	4·11	16·42		0·05	100·00
5	47·31	—	24·19	3·40	0·22	2·80	13·75	5·48	2·86	100·01
6	56·86	—	15·55	8·47	0·28	1·90	1·93	14·63	—	99·62
7	53·10	0·81	22·50	5·10	0·15	2·15	8·49	6·48	1·65	100·43
8	27·73	—	14·50	28·11	8·64	16·85	3·84	3·33	1·01	100·01
9	65·20	—	16·25	5·45	1·87	7·55	2·87	0·50	0·65	100·34

The quartz-augite-diorite forms a massive and extensive mountain range. It is a blackish-green, medium-grained rock, composed in the first line of plagioclase and quartz, then of light-green, partly rhombic, partly monoclinic augite, some hornblende and biotite, and, curiously enough, scapolite, in the form of local deposits, wholly subordinate to these are apatite, magnetite, and pyrites. The composition of the

hydrochloric acid extract proving the admixture of scapolite is shown in analysis (8); the complete analysis in (9). J. P. L.

Hot Springs at Wiesbaden. By R. FRESENIUS (*J. pr. Chem.* [2], **37**, 465—468).—The author gives a detailed analysis of the water from one of these springs (Kleine Schützenhoff). Its temperature was 45.2° on August 20, 1886, the air temperature being 24.8°. A comparison of the composition of this water with that of two of the other springs, analysed in 1879 and 1885 respectively, shows but slight variations in the constituents. A. G. B.

Organic Chemistry.

Formation of Petroleum. By C. ENGLER (*Ber.*, 21, 1816—1827). The theory that petroleum originates from the decomposition of animal matter under high pressure, and at a comparatively low temperature is supported by the author's experiments.

When train-oil is distilled under about 10 atmospheres pressure, which, however, during the operation sank to 4 atmospheres pressure, at an initial temperature of 320° , and a final temperature of slightly above 400° , combustible gases are evolved, and the distillate separates into a lower aqueous, and an upper oily layer. The latter is collected in fractions, and those which are found to contain considerable quantities of unsaturated fatty acids are redistilled. About 60 per cent. of an oily distillate is thus obtained; it has a brownish colour, and in thin layers is transparent with a strong green fluorescence, and a not disagreeable smell. When this oil, which contains more than 90 per cent. of hydrocarbons, is fractioned, and the portion boiling below 150° treated consecutively with concentrated sulphuric acid and a mixture of concentrated sulphuric acid and fuming sulphuric acid, it loses about 37 per cent. by volume. Primary pentane, primary hexane, and primary heptane, were isolated from the residual oil. Primary octane and primary nonane were also present, and probably the mixture also contained secondary hydrocarbons.

When triolein is distilled at about 350° under pressure it yields water, and a mobile oily product, which evolves gas at the ordinary temperature, begins to boil at about 30° , and contains approximately 50 per cent. of compounds boiling below 300° . The residual triolein yields the same products when it is again distilled, so that by repeating the process several times it can be almost wholly converted into volatile and gaseous products.

Tristearin, similarly treated, gives about 60 per cent. of oil, boiling below 300° . Oleic acid and stearic acid, when repeatedly distilled at 350° , under pressure, yield products quite similar to those obtained from triolein and from train-oil. When stearic acid is heated at 350° for several hours in a bent sealed tube, the whole of which is

placed in a digester, it remains unchanged, only when one limb of the tube, being outside the digester, allows condensation to take place, is the acid decomposed. On the other hand, oleic acid and train-oil are decomposed even when the whole of the tube is equally heated.

When train-oil is distilled under diminished pressure, four-fifths of its weight passes over, and the distillate solidifies to a bright yellow, buttery mass, which only contains about 10 per cent. of hydrocarbons. Combustible gases are evolved during distillation, but only a very small quantity of water is formed. F. S. K.

Bromination of Heptane. By F. P. VENABLE (*Amer. Chem. J.*, **10**, 237—239).—The statement of Schorlemmer that by the action of bromine on normal paraffins only secondary bromides are obtained, is examined, and it is shown that by treating hot heptane with liquid bromine, the secondary bromide is the principal product; that gaseous bromine produces almost equal quantities of the primary and secondary bromides, and that when bromine is dissolved in heptane and allowed to act in the cold, dibromheptanes are the principal products. Both here and in the other methods of bromination, the secondary bromide was never formed alone. H. B.

Action of Chlorous Anhydride on Heptylene. By R. G. GRISSOM (*Amer. Chem. J.*, **10**, 225—229).—The absorption of the gas is very energetic, and the temperature must be kept low. A small quantity of the product dissolves in water, and this proves to be due to the presence of acetic acid, a solid crystalline acid containing chlorine, and also probably of other fatty acids. The oil insoluble in water was fractionated, but its examination is incomplete; it appears to contain the chlorhydrin $C_7H_{13}ClO$. The heptylene was obtained from heptane from *Pinus sabiniana*. H. B.

Conversion of Cœnanthylidene and Caprylidene into Isomeric Hydrocarbons by Means of Alcoholic Potash. By A. BÉHAL (*Bull. Soc. Chim.*, **49**, 581—584).—*Methylbutylacetylene*, $C_4H_5C: CMe$, is formed when cœnanthylidene is heated at 140—150° with alcoholic potash for 24 hours. It boils at 112—113° (750·4 mm. pressure), has the specific gravity 0·7632, and does not combine with cuprous chloride nor with an alcoholic solution of silver nitrate. It combines, however, with mercuric chloride, and yields a methylacetone when treated with sulphuric acid.

When chlorcœnanthylene is heated at 140—150° with alcoholic potash for 66 hours, a small quantity of cœnanthylidene still remains unchanged, but when chlorocaprylene is treated similarly, no caprylidene is present in the product.

When caprylidene is boiled with alcoholic potash for 36 hours, it is completely converted into a hydrocarbon, which is identical with that obtained from caprylene, and, like the latter, does not precipitate cuprous or silver salts, but combines with mercuric chloride and yields a methylacetone when hydrated.

The caprylidene prepared from caprylene (compare *Bull.*, **48**, 704) is probably a hydrocarbon of the true acetylene series. F. S. K.

Alcoholic Silver Nitrate as Reagent for Hydrocarbons of the Acetylene Series. By A. BÉHAL (*Bull. Soc. Chim.*, **49**, 335—337).—Large quantities of hydrocarbons of the acetylene series contained in a mixture are often undetected by an ammoniacal solution of cuprous chloride or silver nitrate. A 95°, saturated, alcoholic solution of silver nitrate is, however, a most sensitive reagent, but an excess of the solution must be avoided, as the precipitate is sometimes soluble in presence of a large quantity of the reagent. The compounds obtained are mostly crystalline, and seem to be less alterable than those produced with an aqueous ammoniacal solution, from which they also differ in constitution. They are very sparingly soluble in ammonia, especially when they have been prepared for some time, but as a rule no precipitate is formed with an ammoniacal alcoholic solution of silver nitrate.

The precipitate obtained with œnanthylidene contains nitric acid, and has the composition $C_7H_{11}Ag_2NO_3$; it crystallises in acicular prisms, deflagrates when heated, but does not explode by concussion. It blackens when dried at 100° in the air.

The precipitate obtained with acetylene also contains nitric acid, but does not seem to be a definite compound. It is a yellow substance, which explodes by concussion. Substituted hydrocarbons of the acetylene series gave negative results. F. S. K.

Preparation of Isopropylacetylene from Methyl Isopropyl Carbonyl. By A. BÉHAL (*Bull. Soc. Chim.*, **49**, 23—27).—*Isopropylacetylene*, $Me_2CH:C:CH$, is prepared by treating methyl isopropyl ketone (dimethylacetone) with phosphorus pentachloride, heating the mixture of chlorides obtained at 130—140° for about six hours with about 10 times its volume of alcoholic potash, and fractioning the product. It is a liquid, and seems to boil at about 30°. It combines instantly with an ammoniacal solution of silver nitrate, forming a white compound, C_6H_7Ag , which crystallises from boiling alcohol in prismatic needles. F. S. K.

Methyliodoform. By P. DE BOISSIEU (*Bull. Soc. Chim.*, **49**, 16—17).—*Methyliodoform*, $CMeI_3$, is prepared by adding the calculated quantity of methylchloroform drop by drop to a carbon bisulphide solution of aluminium iodide; the yield does not exceed 25 to 30 per cent. It crystallises from alcohol in small, yellow octahedra, which melt at 95° with decomposition, is readily soluble in carbon bisulphide, benzene, and ether, rather more sparingly soluble in light petroleum, and sparingly soluble in cold ether. It smells like weak iodoform, and partially decomposes when crystallised from solvents other than alcohol. F. S. K.

Decomposition of Potassium Cyanide. By I. H. MANNING (*Amer. Chem. J.*, **10**, 235—236).—The conclusion of v. d. Pfordten that the decomposition and discoloration of strong potassium cyanide

solutions is to be attributed to the action of carbonic acid is not tenable, as shown by Wilkes and confirmed by the author.

H. B.

Potassium Platinocyanide. By T. WILM (*Ber.*, 21, 1434—1454), —When a very small quantity of pure nitric acid (sp. gr. about 40° Beaumé) is added to a few drops of a concentrated solution of potassium platinocyanide, the mixture becomes yellowish and, as long as no excess of nitric acid is present, bright yellowish-brown, slender needles, with a copper-coloured lustre, crystallise from the solution; when more nitric acid is added, the crystals redissolve, the solution becomes colourless, and oily drops separate, often without either warming or concentrating the solution. When the whole is evaporated several times with water and exposed to the air, it crystallises to a mass of needles, but no pure product is obtained. When pure nitric acid is added drop by drop to a concentrated solution of potassium platinocyanide, the mixture becomes yellow; after keeping for some time, copper-coloured, lustrous needles separate. This product is washed with cold water, then with alcohol, and dried in the air; it was found to be the chloride, $3[\text{K}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}]\cdot\text{Cl}$, the chlorine originating from some impurity in the potassium platinocyanide. The compound $3[\text{K}_2\text{Pt}(\text{CN})_4]\cdot\text{KCN}\cdot\text{Pt}(\text{CN})_3 \cdot 6\text{H}_2\text{O}$ is obtained in the form of dark-yellow crystals when pure potassium platinocyanide is treated with nitric acid, as described above (compare *Abstr.*, 1886, 605).

Hydrogen peroxide has no action on a concentrated solution of potassium platinocyanide even when the mixture is warmed, but if a little hydrochloric acid is added to the mixture, the chloride (see above) separates after a short time in bright, copper-coloured crystals. If the solution is evaporated after acidifying with hydrochloric acid and adding more hydrogen peroxide, or if the mother-liquor from the chloride is treated similarly, not a trace of the copper-coloured salt separates, but a colourless, or yellowish, crystalline mass is obtained, which contains the perchloride $\text{K}_2\text{Pt}(\text{CN})_4\text{Cl}_2$.

The bromide is obtained in dark, lustrous needles and prisms when potassium platinocyanide is treated similarly with hydrobromic acid and hydrogen peroxide, but when the mixture is evaporated with an excess of hydrogen peroxide, the perbromide alone is obtained. This is the best method of preparing the bromide, but an excess of hydrobromic acid must be avoided. The pure bromide forms darker needles than those of the chloride; the former crumbles partially on exposure to the air, and when dried becomes white and opaque, but the chloride is stable in the air, and turns a darker greenish-brown when dried.

When pure concentrated sulphuric acid is added drop by drop to a well-cooled, concentrated solution of potassium platinocyanide, hydrogen potassium sulphate separates and the liquid becomes yellow. When the solution is filtered and the residue washed with alcohol, orange-red needles with a violet tint crystallise at the surface of contact of the yellow filtrate and the alcohol, but on adding more alcohol, the crystals are redissolved. Yellowish-red needles with a deep violet to steel-grey tint can be observed when a portion of the mixture is evaporated and examined under the microscope on a warm

glass, but they soon become pale yellow and deliquesce to an oily liquid, which when treated with absolute alcohol crystallises to a mass of orange-red needles. On account of the extreme solubility of this compound in water, alcohol, and ether, it could not be obtained pure.

The action of a mixture of sulphuric acid and hydrogen peroxide on potassium platino-cyanide seems to be influenced by the temperature and by the concentration or quantity of the reagents. When sulphuric acid is gradually added to a well-cooled mixture of a concentrated solution of potassium platino-cyanide and hydrogen peroxide, slender, dark brown, lustrous needles separate after a few hours' time. This product was washed with water, then with alcohol, and dried in the air, but its composition could not be ascertained. A second experiment, in which pure potassium platino-cyanide was employed, yielded the same dark brownish-yellow needles. The product was obtained in the pure state, and was found to be identical with the compound previously obtained by acting on pure potassium platino-cyanide with nitric acid.

This same compound is obtained when a cold, concentrated solution of pure potassium platino-cyanide is electrolysed; hydrogen is evolved at the negative pole, and a mass of yellowish-brown crystals separates at the positive pole, but no evolution of oxygen is evident. The crystals are washed with water, then with alcohol, and dried in the air.

The constitution of this compound is $3[\text{K}_2\text{Pt}(\text{CN})_4], \text{KCN}, \text{Pt}(\text{CN})_3 + 6\text{H}_2\text{O}$; it liberates iodine from potassium iodide.

The chloride and the bromide referred to above have an analogous constitution, namely, $2[\text{K}_2\text{Pt}(\text{CN})_4], 2\text{KCN}, \text{Pt}(\text{CN})_2\text{Cl} + 9\text{H}_2\text{O}$ and $2[\text{K}_2\text{Pt}(\text{CN})_4], 2\text{KCN}, \text{Pt}(\text{CN})_2\text{Br} + 9\text{H}_2\text{O}$ respectively.

F. S. K.

Metallic Nitroprussides. By T. H. NORTON (*Amer. Chem. J.*, **10**, 222—224).—The following salts are described: $\text{CdFe}(\text{CN})_5\text{NO}$, $\text{Hg}_2\text{Fe}(\text{CN})_5\text{NO}$, $\text{CoFe}(\text{CN})_5\text{NO} + 4\text{H}_2\text{O}$, and $\text{NiFe}(\text{CN})_5\text{NO}$. All are insoluble in water and, with the exception of the cadmium salt, decompose easily; the cobalt salt is thrown down as a crystalline powder, the other three are amorphous.

H. B.

Combination of Aluminium Chloride with Acetonitrile, Chloroacetonitrile, and Trichloroacetonitrile. By P. GENVESSE (*Bull. Soc. Chim.*, **49**, 341—343).—The compound $\text{CNMe}, \text{Al}_2\text{Cl}_6$ separates as a white, crystalline powder, when aluminium chloride is added gradually to acetonitrile kept cold by water at the ordinary temperature. When heated, it partially decomposes, becomes pasty, and melts to a brown liquid which solidifies to a resinous product on cooling. On continued heating, or when treated with water, it is completely decomposed. The compound $\text{CN} \cdot \text{CH}_2\text{Cl}, \text{Al}_2\text{Cl}_6$ is obtained by adding chloroacetonitrile gradually to aluminium chloride and warming the mixture. The product melts to a greyish-brown liquid which crystallises on cooling. It is very readily soluble in benzene, melts about 38° , and decomposes when heated or when treated with water.

The compound $\text{CN} \cdot \text{CCl}_3 \cdot \text{Al}_2\text{Cl}_6$ is formed when aluminium chloride is added gradually to trichloroacetonitrile. It is a white, crystalline substance, which quickly decomposes when heated, and has no well-defined melting point. It is sparingly soluble in benzene, and is decomposed when treated with water. F. S. K.

Compound of Methyl Alcohol and Potash. By C. GÖTTIG (*Ber.*, 21, 1832—1835).—The compound $5\text{CH}_3\text{O} \cdot 3\text{KOH}$, obtained when a methyl alcoholic solution of potash is evaporated, crystallises in transparent, elastic plates melting at about 110° , which, when placed on water, move about rapidly on the surface and are decomposed. When kept in a desiccator over sulphuric acid, it gradually gives up the greater part of its alcohol and becomes opaque, but does not entirely lose its property of moving about on the surface of water. F. S. K.

Derivatives of Isodulcitol. By W. WILL and C. PETERS (*Ber.*, 21, 1813—1815).—A lactone, $\text{C}_6\text{H}_{10}\text{O}_5$, is produced when isodulcitol is treated with bromine in aqueous solution. It crystallises in needles, melts at 148° , and is readily soluble in alcohol and water, but sparingly soluble in ether. It behaves similarly to saccharin, but differs from the latter in melting point, solubility, rotatory power, and crystalline form. An oily mixture of a lactone, boiling at 206 — 212° , and a liquid, fatty acid is obtained when it is boiled with concentrated hydriodic acid and a little phosphorus. It yields amorphous *calcium isodulcitate*, $(\text{C}_6\text{H}_{11}\text{O}_6)_2\text{Ca}$, when boiled with calcium carbonate; the *barium* salt, prepared similarly, is also amorphous.

The authors also prepared isodulcitolcarboxylic acid, its barium and calcium salt, and the corresponding lactone melting at 169° . (Compare Fischer and Tafel, this vol., p. 806). F. S. K.

Rotatory and Reducing Power of Lactose. By G. DENIGÈS and E. BONNANS (*J. Pharm.* [5], 17, 363—367, 411—414).—The figures given by different authors for the rotatory power of lactose vary considerably. In a recent work, Schmöger gives results obtained with solutions containing 4 to 36 per cent. at a temperature t for lactose hydrate as $\alpha = 52^\circ.53 + (20 - t) \times 0.055$, which for anhydrous lactose is $\alpha = 55^\circ.30$ at 20° . The results obtained by the authors after three or more crystallisations of the lactose agree perfectly with Schmöger's results. In both cases the penumbra polarimeter with monochromatic light was employed. The rotation is strictly proportional to the dilution of the solution, and the correction for temperature is also dependent on the dilution; thus the correction for a deviation ρ at temperature t , to get the deviation at 20° is

$$x = \rho \frac{\rho}{1000} \times (20 - t) = \rho \times \frac{1020 - t}{1000}.$$

The results obtained with Soleil's saccharimeter are 4° to 6° higher than those given above.

There is considerable diversity in the published results as to the reducing power of lactose. 10 c.c. of Fehling's solution diluted to

20 c.c. and reduced by 0.049 gram of glucose is equally reduced by 70.2 c.c. of hydrated lactose solution of 1 gram per litre. Hence 5 grams glucose is equivalent to 7.16 grams hydrated lactose, or to 6.8 grams anhydrous lactose. Fehling's solution prepared from different formulæ gives the same result. J. T.

Mannose. By E. FISCHER and J. HIRSCHBERGER (*Ber.*, **21**, 1805—1809).—Mannosephenylhydrazone, $C_{12}H_{18}N_2O_5$ (Abstr., 1887, 567), is prepared by heating 200 grams of mannitol dissolved in 1300 c.c. of water with 650 c.c. of nitric acid (sp. gr. = 1.4) for eight hours at 42°. After one or two days, soda is added to neutralise the greater portion of the nitric acid, whilst the nitrous acid is got rid of by adding about 30 grams of urea. The mixture is then completely neutralised with soda and treated with a solution of 100 grams of phenylhydrazine in very dilute acetic acid. After half an hour, it is filtered from the crystalline precipitate, which is washed with water, pressed, and then washed with acetone, after which it is colourless. It crystallises from water in very slightly yellowish, slender prisms soluble in 80 to 100 parts of hot water, much less soluble in alcohol and acetone. It melts between 195° and 200° (not 188°). The dilute hydrochloric acid solution is laevorotatory.

Mannose, $OH \cdot CH_2 \cdot CH(OH) \cdot CO \cdot CH(OH) \cdot CH(OH) \cdot CH_2 \cdot OH$, is obtained by dissolving the above phenylhydrazone in four parts of hydrochloric acid (sp. gr. = 1.19) cooled with ice and salt. After a quarter of an hour, the product is filtered from the phenylhydrazine hydrochloride which separates, treated with twice the volume of ice-water, and neutralised with lead carbonate. The filtrate, which contains, besides mannose, lead chloride and phenylhydrazine, is freed from the latter substances and evaporated in a vacuum. It is then dissolved in absolute alcohol and precipitated with absolute ether. It forms a light yellow syrup having all the properties of the glucoses; it has a sweet taste, dissolves readily in water and alcohol, reduces Fehling's solution, and yields humic substances when heated with 20 per cent. hydrochloric acid. The aqueous solution is dextrorotatory, but much less so than dextrose. When a 10 per cent. solution of mannose is treated with 2 per cent. sodium amalgam, mannitol is formed.

Phenylmannosazone, $C_{18}H_{22}N_4O_4$, is formed when mannosephenylhydrazone (1 part), phenylhydrazine hydrochloride (3 parts), sodium acetate (4 parts), and water (80 parts), are heated at 100—105° for 4 to 5 hours. It crystallises from alcohol in slender, yellow needles, generally grouped in globular aggregates, and melts at 210°.

N. H. M.

Glycogen in Lower Animals: Compounds of Glycogen with Sulphuric Acid. By F. ANDERLINI (*Chem. Centr.*, 1888, 451—452, from *Atti. R. Inst. Veneto* [6], **5**, 1291—1294).—The author has been able to extract glycogen from *Bombyx mori* in the different periods of its life. The greatest amount was found in the chrysalis; a little less in the female butterfly. A small quantity of glycogen was also found in *Blatta orientalis*.

Concentrated sulphuric acid dissolves glycogen in the cold without

perceptible coloration. When, after prolonged standing, the solution was diluted with water, neutralised with barium carbonate, and concentrated in a vacuum, amorphous residues were obtained, the aqueous solution of which became turbid on heating. Glycogen dissolves also in chlorosulphonic acid; the solution of 1 part in 6 to 7 parts chlorosulphonic acid, becomes sticky after 24 to 28 hours, later solid and crystalline. This substance, when dried on porous plates, forms colourless, very hygroscopic crystals, which readily decompose when exposed to the air. The amorphous lead and barium salts are obtained by evaporating the solution which has been neutralised with lead and barium carbonates respectively.

J. W. L.

Succinenylamidoxime and some of its Derivatives. By F. SEMBRITZKI (*Chem. Centr.*, 1888, 623—624).—*Succinenylamidoxime*, $C_2H_4[C(NH_2):N\cdot OH]_2$, is obtained by mixing equivalent quantities of hydroxylamine hydrochloride and sodium carbonate with an alcoholic solution of cyanobenzoic acid; it melts with blackening and disengagement of ammonia at 188° , is soluble in hot water, only slightly soluble in alcohol, and insoluble in chloroform, benzene, and light petroleum. It forms both acid and basic salts. The acetyl-derivative melts at 167 — 168° . The benzoyl-derivative melts at 192° , and when heated with water in a sealed tube at 150° to 160° for five hours, furnishes *succinenylazoxybenzene*, $C_2H_4C_2\left(\begin{smallmatrix} NO \\ N \geq CPh \end{smallmatrix}\right)_2$, melting at 158° to 159° .

Succinenylamidoxime ethyl ether, $C_2H_4[C(NH_2):NOEt]_2$, results from the reaction of succinenylamidoxime, ethyl iodide, and sodium ethoxide, and melts at 119° .

Succinenyluramidoxime, $C_2H_4[C(N\cdot OH):NH\cdot CO\cdot NH_2]_2$, was prepared from equivalent proportions of succinenylamidoxime and potassium cyanate in concentrated watery solution. It contains water of crystallisation, which is given off at 100° to 105° ; when anhydrous it melts with browning and decomposition at $163\cdot5^\circ$.

If an alcoholic solution of cyanosuccinic acid is digested with hydroxylamine and sodium carbonate, and then evaporated to the point of crystallisation on a water-bath, *succinenylimidoxime*, $C_2H_4<\begin{smallmatrix} C(NO\cdot H) \\ C(NO\cdot H) \end{smallmatrix}>NH$, separates out. This substance, dissolved in soda, gives first a blue and then a green colour; with ferric chloride it gives a dark violet coloration. The *benzoyl*-derivative melts at 187 — 189° , the *acetyl*-derivative at 170 — 171° .

J. P. L.

Acetals of Normal Propyl Glycol. By H. LOCHERT (*Bull. Soc. Chim.*, 49, 352—354).—The compound, $CH_2<\begin{smallmatrix} CH_2\cdot O \\ CH_2\cdot O \end{smallmatrix}>CHMe$, is obtained by heating a mixture of acetaldehyde (1 mol.) with propyl glycol (2 mols.) and fractioning the product. It is a colourless liquid which boils at 110 — 112° (768·6 mm. pressure), and has a slight smell of acetaldehyde; it dissolves in $1\frac{1}{2}$ times its volume of water, and is very readily soluble in alcohol and ether. It is separated from its aqueous solution by calcium chloride. Caustic alkalis do not act on

the dry compound, but it yields acetaldehyde and propyl glycol when heated with water in sealed tubes, or, more quickly, when treated with alkalis or acids.

The compound, $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{O} \\ \text{CH}_2 \cdot \text{O} \end{smallmatrix} > \text{CH} \cdot \text{C}_4\text{H}_9$, is obtained similarly from propyl glycol and valeraldehyde. It is a colourless, mobile liquid which boils at 164—166°, and has a faint smell of valeraldehyde. It is almost totally insoluble in water, and resembles the preceding compound in all its properties.

F. S. K.

Methylhydrazine. By G. v. BRÜNING (*Ber.*, **21**, 1809—1810).—*Nitrosomethylcarbamide*, $\text{NH}_2 \cdot \text{CO} \cdot \text{NMe} \cdot \text{NO}$, prepared by treating a cold, neutral, aqueous solution of methylcarbamide with sodium nitrite, crystallises in yellowish leaves, melts at 123—124° with decomposition, and is readily soluble in alcohol and warm water. It is decomposed by continued boiling with water, and is to a large extent converted into methylhydrazinecarbamide when treated with zinc and acetic acid in alcoholic solution.

Methylhydrazine sulphate, $\text{NHMe} \cdot \text{NH}_2 \cdot \text{H}_2\text{SO}_4$, is obtained when the alcoholic solution of methylhydrazinecarbamide is evaporated with hydrochloric acid and the residue heated at 100° with concentrated hydrochloric acid. It crystallises from alcohol in shining needles. The free base is a colourless liquid with a strongly ammoniacal smell; it shows all the reactions of ethylhydrazine.

F. S. K.

Action of Silicon Tetrafluoride on Acetone. By T. H. NORTON and J. H. WESTENHOFF (*Amer. Chem. J.*, **10**, 209—213).—Silicon tetrafluoride was passed into acetone, and the product distilled fractionally; a large proportion of the acetone was unaltered, the fractions boiling higher than acetone and below 90° all decomposed readily after a time, and the only portions that were stable and were analysed were two distilling between 90° and 100°, their specific gravities were 0.904 and 1.36. The analyses present, however, many difficulties as regards the determination of silicon, fluorine, and oxygen; the lighter liquid contains about 11 per cent. of hydrogen, 62.5 per cent. of carbon, and 2 per cent. of silicon, with seemingly no fluorine; whilst the heavier contains 10 per cent. of hydrogen, 10 per cent. of carbon, 5.5 per cent. silicon, and large quantities of fluorine and probably oxygen.

H. B.

Bromination of Acetone: Action of Monobromacetone on Ammonium Thiocyanate. By T. H. NORTON and J. H. WESTENHOFF (*Amer. Chem. J.*, **10**, 213—216).—The additive product of acetone and bromine described by Linnemann could not be obtained, nor could more than 50 per cent. of the acetone be converted into dibromacetone, whereas Mulder has reported that tetrabromacetone is obtainable. Whilst chloracetone and ammonium thiocyanate easily react to yield the thiocyanate of thiocyanisopropimine, bromacetone does not, or at any rate the product of the reaction cannot be isolated from the tarry matters formed.

H. B.

Action of some Organic Acids on Ethyl Oxalate. By LORIN (*Bull. Soc. Chim.*, **49**, 344—345).—Oxalic acid, formic acid, and acetic acid act on normal ethyl oxalate at 140°, and under absolutely similar conditions, forming the ethyl salt of the acid employed and ethyl formate with evolution of carbonic anhydride and small quantities of carbonic oxide. In the case of oxalic acid, the yield of ethyl formate is twice as large as with acetic or formic acid. Benzoic acid and ethyl oxalate do not react even at 240°. F. S. K.

Action of Silver on Ethyl Dibromosuccinate. By J. GORODETZKY and C. HELL (*Ber.*, **21**, 1801—1802).—Ethyl dibromosuccinate dissolved in light petroleum (b. p. 60—70°) is slightly warmed with an equal amount of dry, finely-divided silver (prepared by reducing silver chloride with iron) for two to three hours. The liquid is poured off from the silver bromide and again warmed with silver until no more action takes place. The product of the reaction is pure ethyl fumarate. N. H. M.

Ethyl Cyanosuccinate and Ethyl Cyanotricarballylate. By A. HALLER and L. BARTHE (*Compt. rend.*, **106**, 1413—1416).—A mixture of ethyl cyanacetate, sodium ethoxide, and ethyl monochloracetate, in equivalent proportions, dissolved in excess of alcohol, was boiled until the liquid was no longer alkaline. It was then filtered to remove sodium chloride, heated to expel excess of alcohol, treated with ether, and the product distilled in a vacuum. *Ethyl cyanosuccinate*, $\text{COOEt}\cdot\text{CH}_2\cdot\text{CH}(\text{CN})\cdot\text{COOEt}$, is a colourless, oily liquid which boils at 157—160° under a pressure of 14 mm., and is insoluble in water, but soluble in alcohol, ether, and alkalis. With sodium ethoxide it yields a derivative, $\text{COOEt}\cdot\text{CH}_2\cdot\text{CNa}(\text{CN})\cdot\text{COOEt}$.

In the preparation of the preceding compound a product is obtained which boils at 185—200°, and crystallises in the receiver, or may be crystallised by strongly cooling the distillate. This is *ethyl cyanotricarballylate*, $\text{COOEt}\cdot\text{C}(\text{CN})(\text{CH}_2\cdot\text{COOEt})_2$, which can be purified by recrystallisation from alcohol, and forms hard, white crystals, which melt at 40—41°, and dissolve in alcohol and ether, but are insoluble in water or alkalis. It is probable that in the preparation of the cyanosuccinate some ethyl cyanosodiosuccinate is formed, and this reacts with the chloracetate to form the cyanotricarballylate. The latter can actually be prepared from the cyanosuccinate, sodium ethoxide, and ethyl monochloracetate.

Cyanotricarballylic acid is the mononitrile of isoallylenetetra-carboxylic acid. C. H. B.

Influence of Certain so-called Negative Radicles on the Functions of Certain Groups. By A. HALLER (*Bull. Soc. Chim.*, **49**, 31—36; compare V. Meyer, this vol., p. 147, and Haller, *Abstr.*, 1882, 1189).—The author in his investigations on the influence of certain radicles on the functions of certain groups, has prepared ethyl cyanomalonate, ethyl acetylcyanacetate, ethyl benzoylcyanacetate, and the propionyl, butyryl, orthotolyl, and phenylacetyl-derivatives of ethyl cyanoacetate by treating the sodium compound of ethyl

cynoacetate with acid chlorides. The orthotoluy- and phenylacetyl derivatives yield cyanoketones when treated with boiling water.

Ethyl sodiocyanacetate and ethyl chloracetate yield a crystalline compound which is probably ethyl cyanosuccinate. Metallic sodium dissolves in methyl phenylacetate when the mixture is gently warmed.

When the lead salt of phenylaceticorthocarboxylic acid is distilled, carbonic anhydride and a reddish-coloured liquid, boiling above 200° , are produced.

A resinous product is obtained when ethyl orthonitrophenylacetate is treated with sodium ethoxide.

Ethyl succinimidoacetate yields a sodium-derivative which reacts with benzoic chloride.

Ethyl trichlorolactate shows an acid reaction with turnesole, and reduces ammoniacal silver and Fehling's solutions; its acetyl-derivative has none of these properties, and is quite insoluble in alkalis.

F. S. K.

Molecular Refraction of the Isomerides Fumaric and Maleic Acids; Citraconic, Itaconic, and Mesaconic Acids, and of Thiophen. By C. KNOPS (*Chem. Centr.*, 1888, 464—465, from *Verh. nat. Ver. Bonn*, 1887, 17).—The isomeric compounds which cannot be explained by the theory of valency, such as the physical isomerides and such isomerides as seem to have the same chemical composition yet yield different derivatives when treated with the same reagents (optically active and optically inactive substances), were compared by the author with reference to those physical properties which appeared to be correlated to substances of known constitution.

From his experiments it follows that fumaric and maleic acids, on the one hand, and mesaconic and citraconic acids on the other hand, probably possess different structures. The author also submits a new formula for thiophen. No details are given.

J. P. L.

Action of Normal Alkaline Tungstates on Solutions of Tartaric Acid. By D. GERNEZ (*Compt. rend.*, 106, 1527—1530; compare *Abstr.*, 1887, 540, and this vol., p. 97).—Crystallised sodium tungstate, Na_2WO_4 , was added to 1.25 gram of tartaric acid in quantities varying from one-fortieth to 17 mols. per molecule of acid, the proportion of water being sufficient to make the volume of the liquid up to 50 c.c. The rotatory power of the solution increases with the proportion of tungstate until the salt and the acid are present in equal molecular proportions. It then increases more and more slowly until 2 mols. of the salt are present for each molecule of acid, beyond which point the rotatory power decreases by gradually diminishing quantities. These facts indicate the formation of a compound of 1 mol. tartaric acid and 1 mol. sodium tungstate and a second compound containing 1 mol. of the acid and 2 mols. of the tungstate; the maximum rotatory power being 22 times as great as that of the tartaric acid in the solution. When further quantities of the tungstate are added, the compound of the salt and the acid is gradually dissociated.

With potassium tungstate, the phenomena indicate the formation of a compound of 1 mol. of the tungstate and 1 mol. of tartaric acid,

the maximum rotation being 23 times as great as that of the tartaric acid in the solution. C. H. B.

Action of Chlorine on Sulphonic and Oxythio-derivatives of Heptyl. By W. SPRING and C. WINSSINGER (*Bull. Soc. Chim.*, **49**, 68—74; compare Abstr., 1884, 1127).—*Dichlorheptylsulphonic acid* is formed by acting on normal heptylsulphonic acid with chlorine in direct sunlight for seven to eight hours; not a trace of sulphuric acid is formed during the reaction. The *barium* salt has the formula $(C_7H_{13}Cl_2SO_3)_2Ba$.

Trichlorheptylsulphonic acid is prepared by treating the preceding compound with chlorine until no further action takes place. It is readily decomposed by boiling water with formation of sulphuric acid and a chlorheptyl-derivative.

Hexachlorhydroxyheptylic acid, $C_7H_5Cl_6O_3$, is obtained when heptylsulphonic acid is heated with iodine trichloride at 167 — 170° ; it is insoluble in water.

Pentachlorheptylic acid, $C_7H_5Cl_5O_2$, and trichlorheptylsulphonic acid, identical with the trichloro-derivative described above, are also produced by the same reaction. Both compounds are soluble in water, and yield barium salts which crystallise together to form a substance, $2(C_7H_{12}Cl_3SO_3)_2Ba, 3(C_7H_5Cl_3O_2)_2Ba + 24H_2O$.

When heptyloxysulphide is treated with chlorine in presence of water, an oily product is obtained, about two-thirds of which is soluble in soda. Trichloro- and tetrachloro-heptane were isolated from the insoluble residue; both compounds give silver cœnanthylate, cœnanthaldehyde, a small quantity of heptyl cœnanthylate, and a deposit of silver when treated with silver oxide and water at 155 — 162° . The soda solution yielded a mixture of two barium salts, $2(C_7H_{14}ClSO_3)_2Ba, (C_7H_{13}Cl_2SO_3)_2Ba$ and



these were separated by crystallisation.

F. S. K.

3 : 4-Thioxen and Tetramethylthiophen. By N. ZELINSKY (*Ber.*, **21**, 1835—1839).— $\beta\beta$ -Thioxen, $C_4SH_2Me_2$ [$Me_2 = 3 : 4$], is obtained when a mixture of sodium dimethylsuccinate and phosphorus trisulphide is distilled. It is a transparent, strongly refractive oil which boils at 144 — 146° (762 mm. pressure), and has a characteristic thiophen-like smell. A trace of this compound, dissolved in concentrated sulphuric acid, gives an intensely emerald-green solution with isatin; a glacial acetic acid solution gives a greenish-violet coloration with anthraquinone.

From the product obtained by the oxidation of 3 : 4-thioxen an acid was isolated which crystallises in very slender needles, melts at 139° , and is sparingly soluble in cold water, and sublimes.

Tetramethylthiophen, C_4SMe_4 , prepared by converting trimethylthiophen into its iodo-derivative by means of iodine and mercuric oxide and then treating the product with sodium and methyl iodide in ethereal solution, boils at 182 — 184° (uncorr.). The yield is extremely small.

F. S. K.

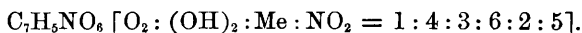
Constitution of Benzene. By A. CLAUS (*J. pr. Chem.* [2], **37**, 455—464; compare *Abstr.*, 1887, 719).—In this paper, the author replies to the criticisms passed by Baeyer on his diagonal formula (*Annalen*, **245**, 120), and maintains that Baeyer's work on terephthalic acid and its hydrogen additive derivatives supports this formula. The author proceeds to explain orientation and the structure of quinone by the help of his formula for the benzene nucleus.

A. G. B.

Iodation of the Phenols by Nitrogen Iodide. By C. WILLGERODT (*J. pr. Chem.* [2], **37**, 446—448).—By the action of nitrogen iodide on dilute alcoholic potassium phenoxide, ammonia is evolved, and triiodophenol is formed together with a little iodophenol. The author describes the best method of handling the nitrogen iodide in order to avoid an accident. Powdered iodine in dilute alcoholic phenol, mixed with ammonia, produces orthiodophenol, together with tri-, di-, and paramono-iodophenol. If β -naphthol be substituted for phenol, iodo- β -naphthol, previously described by Meldola (*Trans.*, 1885, 525), is obtained by both methods, together with two secondary products, one crystallising in needles melting at 223°, the other an amorphous, greyish-white substance. By applying this method to the iodation of the phenols, the author and Kornblum have obtained *iodothymol*, $C_6H_2MePrI \cdot OH$ [1 : 4 : 6 : 3] melting at 69°, and *di-iodorthocresol* melting at 69·5°.

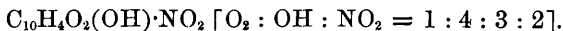
A. G. B.

Action of Alkali Nitrites on Halogen-derivatives of Quinones. By F. KEHRMANN (*Ber.*, **21**, 1777—1783).—When trichlor- or tribrom-orthotoluquinone is digested on a water-bath with potassium nitrite (5 mols.), a heavy, sandy, crystalline precipitate is formed, which, when dissolved in hot water and treated with barium chloride, yields the barium salt of a *nitrodihydroxytoluquinone*,



This when oxidised with cold nitric acid is converted into what is probably the *methylhydroxypentaketone*, $C_6O_5Me \cdot OH$. The latter is dissolved by cold, strong sulphurous acid (similarly to triquinoyl, Nietzki and Benckiser, *Abstr.*, 1885, 781); on neutralising the solution with sodium carbonate, a reddish-yellow liquid is formed containing probably methylrhodizonic acid [$O_3 : OH : OH : Me, OH = 1 : 4 : 5 : 3 : 6 : 2$].

Dichloro- α -naphthaquinone, when heated with an aqueous alcoholic solution of sodium nitrite, yields the sodium salt of Diehl and Merz's nitronaphthalic acid (hydroxynitro- α -naphthaquinone) (*Abstr.*, 1878, 888), which must therefore have the constitution



When this is reduced with stannous chloride, *amidotrihydroxynaphthalene*, [$OH_3 : NH_2 = 1 : 3 : 4 : 2$], is formed. When amidotrihydroxynaphthalene hydrochloride is dissolved in cooled, strong nitric acid, and the whole poured into 10 parts of nearly boiling water, the compound $C_{10}H_4O_3 \cdot N \cdot NO$ [$(OH)_3 : N_2O = 1 : 3 : 4 : 2$], separates in splendid, reddish-yellow needles. The latter dissolves in hot water and alcohol,

but is decomposed by prolonged boiling; nitric acid dissolves it very readily. When heated at 100° it detonates.

Dichloro- α -naphthaquinonesulphonic acid (Claus and S. van der Cloet, this vol., p. 602) is converted by alkali nitrite into a nitrohydroxy- α -naphthaquinonesulphonic acid, $[O_2 : NO_2 : OH = 1 : 4 : 2 : 3]$. The *potassium salt* forms readily soluble, yellow, hair-like needles: the *barium salt* is a yellow, crystalline precipitate, sparingly soluble in cold water.

N. H. M.

Formation of Eugenol from Coniferin. By L. CHIOZZA (*Chem. Centr.*, 1888, 443, from *Rendi. R. Inst. Lombardo* [2], 21, 172).—Coniferin is reduced to eugenol by sodium amalgam in a weak alkaline solution. Some unchanged coniferin is precipitated from the cold solution by adding a little water. Dilute sulphuric acid precipitates the eugenol from the filtered solution. As an intermediate product coniferyl alcohol, $C_{10}H_{12}O_3$, is formed.

J. W. L.

Combinations of Aniline with Cuprous Chloride, Bromide, and Iodide. By A. SAGLIER (*Compt. rend.*, 106, 1422—1425).—2 grams of cuprous chloride was heated in sealed tubes at 100° with 40 c.c. of a mixture of equal volumes of alcohol and aniline. When cooled the liquid deposits white, acicular crystals of the composition $2PhNH_2, Cu_2Cl_2$, which rapidly turn green when exposed to the air. The bromide under similar conditions yields an analogous compound. The corresponding iodine compound forms white needles which become rose-coloured and finally black when exposed to the air.

These compounds are not affected by light, but are decomposed by alkalis with liberation of aniline. They are insoluble in water and alcohol, and alter rapidly when exposed to air, but if freed from excess of aniline, they can be preserved for some time. At 50° they begin to decompose with evolution of aniline, and at a dull red heat a residue of the cuprous salt is left.

When equivalent quantities of cuprous chloride and aniline hydrochloride are heated in sealed tubes with dilute hydrochloric acid until the copper salt is dissolved, the liquid when cooled deposits white crystals of the compound $2PhNH_2Cl, Cu_2Cl_2$, which is more stable than the preceding compounds, but becomes first rose-coloured, then brown, and finally black when exposed to air. Cuprous bromide yields a similar compound which crystallises in lamellæ if the solution is cooled rapidly, and in prismatic needles if it is cooled slowly.

C. H. B.

Action of Fluoride of Silicon on Organic Bases. By A. M. COMEY and C. L. JACKSON (*Amer. Chem. J.*, 10, 165—181).—The action of silicon tetrafluoride on ammonia results in the formation of the compound $2NH_3, SiF_4$ (Gay-Lussac and Thenard); the action on aniline has only been imperfectly studied by Laurent and Delbos and by Knop. It is now shown that additive products of a somewhat different type, namely, $3NH_3X, 2SiF_4$, are formed by the following amines:—Aniline, paratoluidine, orthotoluidine, parachloraniline, diphenylamine, dimethylaniline, quinoline, and dimethylamine, and besides these

aniline and dimethylamine from another compound, of the type $4\text{NH}_2\text{X}_2\cdot 2\text{SiF}_4$. The compound $3\text{NH}_3\cdot 2\text{SiF}_4$ could not be prepared.

Trianiline disilicotetrafluoride, $3\text{NH}_2\text{Ph}\cdot 2\text{SiF}_4$, is formed very readily, is amorphous, sublimes without melting, is decomposed slowly by alcohol, quickly by water with formation of aniline silicofluoride, which is reconverted into the original substance by sublimation. Ammonia decomposes it with formation of the diammoniosilicotetrafluoride of Gay-Lussac. The corresponding compounds of orthotoluidine, paratoluidine, monochloraniline, and parabromaniline, are very similar in all respects; symmetrical tribromaniline undergoes no reaction, neither do diphenylamine, dimethylaniline, or quinoline until they are dissolved in benzene; in the last cases the compounds are crystalline. The tri-dimethylamine-derivative is only obtained by subliming *di-dimethylamine silicotetrafluoride*. This is deposited as a white powder on bringing together its constituents; it is at once decomposed by heat, yielding dimethylamine and the tri-compound. The aniline salt, $4\text{NH}_2\text{Ph}\cdot 2\text{SiF}_4$, is obtained by leading aniline vapour into silicon tetrafluoride, or by heating the trianiline compound with aniline at 150° ; it is not very stable, decomposing even at ordinary temperatures into trianiline disilicotetrafluoride, and aniline; for this reason the simplest empirical formula is doubled.

It is possible that the pyridine and quinoline additive products obtained with silicon tetrachloride by Harden (Trans., 1887, 40) correspond with the above, although they are less stable. H. B.

Action of Phenylamine and Diphenylamine Hydrochlorides on some Fatty Amines. By H. ECKENROTH and J. RÜCKEL (*Chem. Centr.*, 1888, 784, from *Pharm. Zeit.*, **33**, 282).—Phenylurethane does not result from the action of phenylamine hydrochloride on urethane as would be expected, but diphenylcarbamide, $\text{CO}(\text{NHC}_6\text{H}_5)_2$, is formed. From analogy, diphenylamine hydrochloride and urethane should yield tetraphenylcarbamide, but diphenylamine is the only product; the tetraphenylcarbamide may probably be decomposed when in a nascent state by the hydrochloric acid formed by the reaction. J. P. L.

Double Compounds of Acetone with the Sulphites of Aromatic Amines. By P. BOESSNECK (*Ber.*, **21**, 1906—1910).—When sulphurous anhydride is passed into acetone, the gas is absorbed with considerable development of heat. The product, probably $\text{CMe}_2\langle\text{O}\rangle\text{SO}$, when poured into water, sinks, and only mixes with the water when violently shaken with it; when heated, it decomposes into its constituents.

Acetone-aniline sulphite, $\text{CMe}_2\cdot\text{SO}_2\cdot\text{NH}_2\text{Ph}$, is obtained by adding aniline to acetone saturated with sulphurous anhydride, and washing the crystalline product with acetone. If $1\frac{1}{2}$ mol. of alcohol is added to the acetone before treating with aniline, the double compound separates in stellate groups of long, colourless needles. It is very readily soluble in water, soluble in alcohol, and insoluble in water. When kept in closed vessels, it remains for months unchanged.

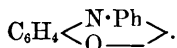
Acetone-dimethylaniline sulphite, $\text{COMe}_2\cdot\text{SO}_2\cdot\text{NMe}_2\text{Ph}$, forms lustrous plates readily soluble in alcohol and water, insoluble in acetone.

Acetone-ethylaniline sulphite, $\text{COMe}_2\cdot\text{SO}_2\cdot\text{NHEtPh}$, forms very large crystals.

Acetone-ethylenetoluylenamidine sulphite, $\text{C}_3\text{H}_6\text{O}\cdot\text{SO}_2\cdot\text{C}_9\text{H}_{10}\text{N}_2$, forms lustrous, rhombic crystals.

Aniline sulphite, $\text{NH}_2\text{Ph}\cdot\text{SO}_2$, can be obtained in well-formed plates by passing sulphurous anhydride through a warm aqueous solution of equal parts of aniline and potash; when removed from the solution, it at once gives off sulphurous anhydride (compare Schiff, *Annalen*, **140**, 133, and **144**, 47). N. H. M.

Derivatives of Paraphenolphenylamine. By E. V. BANDROWSKI (*Monatsh.*, **9**, 133—137; compare *Monatsh.*, 1887, 523).—When paraphenolphenylamine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NHPh}$ (1 mol.) is dissolved in benzene and oxidised with yellow mercuric oxide (2 mols.), two atoms of hydrogen are removed with formation of the compound



This substance crystallises in interwoven masses of a bright red colour melting at 97° . It is extremely soluble in alcohol, ether, chloroform, and benzene, is best recrystallised from light petroleum, and readily decomposes on boiling with water, alkalis, or dilute acids with formation of quinone. In a similar way paraphenoltolylamine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, may be made to yield the compound $\text{C}_6\text{H}_4\langle\overset{\text{N}(\text{C}_6\text{H}_4\text{Me})}{\underset{\text{O}}{\text{—}}}\rangle$, which much resembles its homologue above described. On evaporation of a solution in light petroleum, crystals of a deep red colour and dark green lustre are formed. These melt at 70° , and likewise yield quinone on boiling with water. The author has also isolated the compound $\text{C}_6\text{H}_4\langle\overset{\text{N}(\text{C}_6\text{H}_4\text{Me})}{\underset{\text{N}(\text{C}_6\text{H}_4\text{Me})}{\text{—}}}\rangle$, from paradi-tolylamidobenzene, $\text{C}_6\text{H}_4(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$. G. T. M.

Nitrogenous Quinone-derivatives. By R. NIETZKI and A. W. SCHMIDT (*Ber.*, **21**, 1850—1856).—*Diamidodihydroxyquinone*, $\text{C}_6\text{H}_6\text{N}_2\text{O}_4$, is formed when sodium nitrite is added to a solution of diamidotetrahydroxybenzene hydrochloride, or when a solution of the latter is exposed to the air after neutralising the hydrochloric acid present; after adding alcohol the product is precipitated in reddish-brown needles by means of aniline or sodium acetate. This compound is also produced by the action of phenanthraquinone on a glacial acetic acid solution of diamidotetrahydroxybenzene hydrochloride or by partially oxidising the latter with ferric chloride. After drying at 100° , it contains water which is, however, evolved at 150° . When treated with concentrated hydrochloric acid, it yields a yellowish, crystalline *hydrochloride* which is decomposed by water. When heated with anhydrous sodium acetate and acetic anhydride, it gives a reddish-brown, crystalline compound which is probably a mixture of several acetyl-derivatives.

When a solution of the reddish sodium salt obtained by dissolving hexacyldiamidotetrahydroxybenzene in soda (Nietzki and Benckiser, Abstr., 1885, 779), or of the sodium salt of diacetyldiamidohydroquinone (Nietzki and Preusser, Abstr., 1886, 1024) is treated with hydrochloric acid, *diacetyldiamidodihydroxyquinone*, $C_6(OH)_2O_2(NHAc)_2$, is precipitated in brownish-red needles.

Diacetyldiamidotetrahydroxybenzene, $C_6(OH)_4(NHAc)_2$, is formed when the preceding compound is treated with stannous chloride and dilute hydrochloric acid. It crystallises from alcohol in colourless needles, and is quickly converted into the quinone when its alkaline solution is exposed to the air.

The characteristic reddish needles of the sodium salt of diacetyldiamidodihydroxyquinone separate when the reddish-brown product obtained by heating diamidodihydroxyquinone with sodium acetate and acetic anhydride is dissolved in soda, and the solution kept for some time. The constitution of diamidodihydroxyquinone is therefore $[O_2 : (NH_2)_2 : (OH)_2 = 1 : 4 : 2 : 5 : 3 : 6]$.

Diquinoylimide, $C_6O_4(NH)_2 + 5H_2O$ $[(NH)_2 = 3 : 6]$, is obtained as a bye-product in the preparation of triquinoyl from diamidotetrahydroxybenzene. It is a colourless compound which is insoluble in ordinary solvents, and is decomposed with evolution of gas by boiling with water. It is converted into diamidotetrahydroxybenzene when treated with stannous chloride and hydrochloric acid.

Tetrahydroxyquinoneanilide, $C_6O(OH)_4 \cdot NPh$ $[O : (NPh) = 1 : 4]$, is obtained when hexahydroxybenzene is dissolved in dilute alcohol, aniline added, and the solution exposed to the air. It crystallises in shining, golden leaves which have a carmine-red colour by transmitted light, and are very sparingly soluble in all neutral solvents, but soluble in alkalis with decomposition.

The compound $C_6(OH)_2O_3 \cdot NPh, NH_2Ph$ is obtained in red needles with a superficial green tinge when tetrahydroxyquinone is treated with aniline. *Aniline rhodizonate*, $C_6H_2O_6(NH_2Ph)_2$, separates in red needles when a dilute hydrochloric acid solution of sodium rhodizonate is treated with aniline.

Croconamic acid (Nietzki and Benckiser, Abstr., 1886, 540) forms a *barium* salt which crystallises in sparingly soluble, yellow leaves, and has the composition $C_5HNO_4Ba + 4H_2O$ when dried at 120° . Croconamic acid has therefore the constitution $C_6O_2(OH)_2 \cdot NH$.

F. S. K.

Tautomerism of Thiocarbamides. By F. FOERSTER (*Ber.*, 21, 1857—1873).—*Methyl anisylimidoanisylthiocarbamate*,

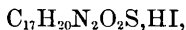


prepared by treating dianisylthiocarbamide with methyl iodide, crystallises from alcohol in small, white prisms, melts at 87° , is readily soluble in hot alcohol and ether, moderately soluble in cold alcohol, and almost insoluble in water. It is readily soluble in sulphuric acid, hydrochloric acid, and acetic acid, moderately soluble in nitric acid and hydrobromic acid, and still less soluble in hydriodic acid. The *hydrochloride*, $C_{16}H_{18}N_2O_2S \cdot HCl$, crystallises in white leaves. The *platinochloride*, $(C_{16}H_{18}N_2O_2S)_2 \cdot H_2PtCl_6$, crystallises in

small, short prisms which are more readily soluble in alcohol than in water. The *aurochloride* is amorphous, and melts under water. When the base is distilled, methylmercaptan and carbodianisylimide are formed. Alkalis decompose it into methylmercaptan and dianisylcarbamide. Treated with alcoholic ammonia, it yields methylmercaptan and *dianisylguanidine*, $C_7H_7O \cdot N:C(NH_2) \cdot NH \cdot C_7H_7O$, and with alcoholic anisidine it gives methylmercaptan and trianisylguanidine, $C_7H_7O \cdot N:C(NH \cdot C_7H_7O)_2$.

Methyl anisylthiocarbamate, $SMe \cdot CS \cdot NHC_7H_7O$, and anisylthiocarbamide are obtained when the base is digested with carbon bisulphide; the former compound is soluble in very dilute alkalis, and is reprecipitated by hydrochloric acid; it is decomposed by concentrated alkalis, and yields anisylthiocarbamide and methylmercaptan when heated.

Ethyl anisylimidoanisylthiocarbamate, $C_{17}H_{20}N_2O_2S$, prepared by treating dianisylthiocarbamide with ethyl iodide, melts at 82.5° , and resembles the corresponding methyl base. The *hydriodide*,



crystallises in large, shining rhombohedra which melt at $162-163^\circ$ with decomposition, and are insoluble in ether. The *platinochloride*, $(C_{17}H_{20}N_2O_2S)_2, H_2PtCl_6$, is similar to the salt of the methyl base.

Propyl anisylimidoanisylthiocarbamate, $C_{18}H_{22}N_2O_2S$, prepared similarly, crystallises in shining leaves melting at 58° . This base and its *platinochloride* closely resemble the corresponding methyl- and ethyl-derivatives.

Ethylene anisylimidoanisylthiocarbamate, $C_7H_7ON:C<\overset{N(C_7H_7O)}{S \cdot CH_2 \cdot CH_2}>$, prepared by heating dianisylthiocarbamide with ethylene bromide, crystallises in white prisms, melts at 128° , is readily soluble in benzene and hot alcohol, less readily soluble in light petroleum, and insoluble in water. The *hydrochloride* and *sulphate* are readily soluble in water, the *hydrobromide* and *hydriodide* are less readily soluble and the *picrate* is only sparingly soluble. The *platinochloride*, $(C_{17}H_{18}N_2O_2S)_3, H_2PtCl_6$, is only stable in the dry state.

Ethylene anisylthiocarbamate, $CS<\overset{N(C_7H_7O)}{S \cdot CH_2 \cdot CH_2}>$, prepared by heating the preceding compound with carbon bisulphide, is a neutral substance which crystallises from alcohol in hard prisms, and from benzene, in which it is readily soluble, in large, transparent crystals melting at 136° , and rather readily soluble in hot alcohol and ether. It is with difficulty converted into the monothio-derivative by mercuric oxide, silver oxide, or silver nitrate, and it combines with methyl iodide to form a crystalline compound, $C_{10}H_{11}NOS_2, MeI$, which melts at about 141° , is soluble in water, alcohol, and benzene, but insoluble in ether. When digested with anisidine, it gives mercaptan and ethylene anisylimidoanisylthiocarbamate.

Ethylene anisylthiocarbamate, $CO<\overset{N(C_7H_7O)}{S \cdot CH_2 \cdot CH_2}>$, prepared by heating the dithiocarbamate with alcohol and chloroacetic acid, crystallises

in shining leaves, melts at 116° , and is readily soluble in alcohol, ether, and benzene, but insoluble in water.

Dianisylthiohydantoïn, $C_7H_7ON:C<\overset{N(C_7H_7O)}{S\cdot CH_2\cdot CO}>$, is obtained when dianisylthiocarbamide is heated with chloracetic acid. It crystallises from glacial acetic acid in bright yellow needles, melts at 190° , is readily soluble in benzene and glacial acetic acid, sparingly soluble in hot alcohol, but insoluble in water or cold alcohol.

Anisyl phenylthiocarbamide, $NHPh\cdot CS\cdot NH\cdot C_7H_7O$, produced by treating phenylthiocarbimide with anisidine, or by the action of anisylthiocarbimide on aniline, crystallises in white prisms melting at 127° . When digested with ethylene bromide, it yields a resinous product from which a crystalline base, $NPh\cdot C<\overset{N(C_7H_7O)}{S\cdot CH_2\cdot CH_2}>$, melting at 143° , was isolated. Two isomeric bases are formed when α -naphthylphenylthiocarbamide is treated with ethylene bromide. The one is sparingly soluble in alcohol, crystallises in needles melting at 184.5° , and yields phenylthiocarbimide and ethylene α -naphthylthiocarbamate when treated with carbon bisulphide; it can also be obtained by the action of aniline on the additive product of methyl iodide and ethylene α -naphthylthiocarbamate; its constitution is, therefore, $NPh\cdot C<\overset{N(C_{10}H_7)}{S\cdot C_2H_4}>$. The other is more readily soluble in alcohol, and crystallises in shining leaves melting at $129-130^{\circ}$; it is, however, impure, as it yields the decomposition products of both the theoretical bases when treated with carbon bisulphide. By acting on the additive product of methyl iodide and ethylene phenylthiocarbamate with α -naphthylamine, the pure compound melting at 134.5° is obtained; it yields naphthylthiocarbimide and ethylene phenylthiocarbamate when treated with carbon bisulphide. Its constitution is, therefore, $C_{10}H_7\cdot N:C<\overset{NPh}{S\cdot C_2H_4}>$.

A base, $NPh\cdot C(SMe)\cdot NHC_7H_7O$, which crystallises in long, white, silky needles melting at 80° , is obtained by the action of methyl iodide on anisylphenylthiocarbamide. It yields phenylthiocarbimide when treated with carbon bisulphide. The base

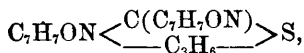


obtained from methyl iodide and α -naphthylphenylthiocarbamide, crystallises in small, white needles which melt at 96° .

Phenyltrihydrothiazole, $NPh<\overset{C_2H_4}{CH_2}>S$, is obtained by reducing an alcoholic solution of ethylene phenylthiocarbamate with zinc and hydrochloric acid. It is an oily base which is readily soluble in alcohol and ether, but insoluble in water; it is volatile with steam, and has a slight smell resembling that of conine.

Trimethylene phenylimidophenylthiocarbamate, $NPh<\overset{C(NPh)}{C_3H_6}>S$, formed by the action of trimethylene bromide on diphenylthiocarbamide, crystallises in white, silky needles, melts at 123° , and behaves similarly to the ethylene base.

Trimethyleneanisylimidoanisylthiocarbamate,



prepared similarly, crystallises from alcohol in well-defined prisms melting at 113–114°.

Methylene phenylimidophenylthiocarbamate, $\text{NPh} < \underset{\text{CH}_2}{\text{C}(\text{NPh})} > \text{S}$, prepared by acting on diphenylthiocarbamide with methylene bromide, crystallises in long needles, melts at 68°, and is very readily soluble in alcohol. The *platinochloride*, $(\text{C}_{14}\text{H}_{12}\text{N}_2\text{S})_2 \cdot \text{H}_2\text{PtCl}_6$, is crystalline.
F. S. K.

Guanidines and Guanidine Cyanides. By L. HIRSCH (*Chem. Centr.*, 1888, 624–625).—If cyanogen gas is led into an ethereal solution of nitrodiphenylguanidine, prepared by desulphurising nitrodiphenylthiocarbamide with ammonia, *nitrodiphenylguanidine dicyanide*, $\text{NH}:\text{C} < \underset{\text{N}(\text{C}_6\text{H}_4\cdot\text{NO}_2)}{\text{NPh} \text{---} \text{C}(\text{NH})} >$, is formed, which decomposes on heating. Dilute hydrochloric acid changes it into *nitrodiphenyloxalylguanidine*, $\text{NH}:\text{C} < \underset{\text{N}(\text{C}_6\text{H}_4\cdot\text{NO}_2)}{\text{NPh} \text{---} \text{CO}} >$, melting at 168°. If an alcoholic solution of this compound is heated with concentrated hydrochloric acid, *nitrodiphenylparabanic acid*, $\text{CO} < \underset{\text{N}(\text{C}_6\text{H}_4\cdot\text{NO}_2)}{\text{NPh} \text{---} \text{CO}} >$, is formed.

Attempts to prepare α -cyanogen additive products by acting on nitrotriphenylguanidine with cyanogen gas failed, nor were any definite substances obtained by reducing the above nitroguanidine with zinc and hydrochloric acid.

β -*Nitrotriphenylguanidine dicyanide*, $\text{C}_{21}\text{H}_{16}\text{N}_6\text{O}_2$, can be obtained by the action of an alcoholic solution of aniline hydrochloride on the cyanogen additive products of the corresponding diphenylguanidine. Reduction of this compound with zinc and hydrochloric acid produces a complete decomposition, aniline, ammonium chloride, and diphenylguanidine being formed.

Bromoguanidine is obtained by acting on phenyl thiocarbimide with parabromaniline, and desulphurising with ammonia. If an ethereal solution of bromodiphenylguanidine melting at 147° is treated with cyanogen gas, *bromodiphenylguanidine dicyanide* is formed, which is converted by acids, even in the cold, into bromodiphenyloxalylguanidine melting at 156°. These two compounds when treated with concentrated hydrochloric acid give bromodiphenylparabanic acid, melting at 194°.

Attempts were made to desulphurise diphenylthiocarbamide with diamines. Phenylenediamine and toluenylenediamine did not produce any characteristic product. Benzidine formed dibenzylthiocarbamide.

When diphenylguanidine dicyanide was treated with amines of the aromatic series, no definite products were formed, only a slightly fluorescent, red coloration. Diphenylamine and cumidine hydro-

chloride react on one another, but no pure product could be separated.

Phenylenediamine and diphenylguanidine dicyanide, both in alcoholic solution, form a product yielding a red hydrochloride. This salt is so insoluble in the various solvents that it is difficult to obtain it pure. Benzidine hydrochloride acts similarly.

If phenyl- β -naphthylthiocarbamide is desulphurised with aniline, triphenylguanidine is formed. J. P. L.

Benzazimide. By H. FINGER (*J. pr. Chem.* [2], **37**, 431—445).—The author applies the name *benzazimide* to the compound $C_7H_5N_3O$, obtained by the action of nitrous acid on orthamidobenzamide, and previously described by Weddige and himself (*Abstr.*, 1887, 667).

Orthamidobenzethylamide, $NH_2 \cdot C_6H_4 \cdot CONH\text{Et}$, is obtained by the action of an alcoholic solution of ethylamine on isatoic acid. It crystallises from benzene in leaflets or feathery needles melting at $104\text{--}105^\circ$. When it is dissolved in hydrochloric or nitric acid and the calculated quantity of sodium nitrite added, *ethyl benzazimide*, $C_6H_4 \cdot \begin{smallmatrix} \text{CO} \cdot \text{NEt} \\ \text{-- N} \cdot \text{N --} \end{smallmatrix}$, separates, at first in oily drops and afterwards in needles, soluble in ether, alcohol, chloroform, and hot water, melting at 70° , and of an agreeable, ethereal odour.

Benzazimide is decomposed by hot, strong alkalis into orthamidobenzoic acid and nitrogen. Strong hydrochloric acid dissolves both benzazimide and methylbenzazimide in the cold without change, but when heated with either of them in a sealed tube at $120\text{--}130^\circ$, nitrogen and a little carbonic anhydride are evolved, a crystalline mass is formed, consisting of chlorosalicylic acid and a little salicylic acid, and ammonia or methylamine is found in solution.

Orthethamidobenzamide, $NEtH \cdot C_6H_4 \cdot CONH_2$ (compare *Abstr.*, 1887, 1044), is obtained when orthamidobenzamide is heated with the calculated quantity of alcoholic ethyl iodide in a sealed tube at 100° . The contents are allowed to remain in the cold for 12 hours, then evaporated to a syrup, and treated with ammonia; the oil thus precipitated gradually solidifies, and is recrystallised from hot water; it melts at $128\text{--}129^\circ$.

Orthonitrosomethamidobenzamide, $NO \cdot NMe \cdot C_6H_4 \cdot CONH_2$, is obtained by the action of nitrous acid on orthomethamidobenzamide, as white needles, which crystallise from hot alcohol in shining, pale-yellow prisms, and from hot water in shining leaflets; it melts at 149° . The *nitrosoethyl*-derivative crystallises from hot water in pale-yellow, prismatic needles melting at 110° . Both of these give Liebermann's colour reaction.

Alcoholic hydrogen chloride in the cold converts orthonitrosomethamidobenzamide into orthomethamidobenzamide and nitrous acid. Aqueous hydrogen chloride produces a mass which gives an intensely green hydrochloride when treated with pure water; this crystallises in green needles, and is not the paranitroso-compound (compare *Abstr.*, 1887, 244, 729).

The foregoing reactions confirm the structural formula already given for benzazimide (*Abstr.*, 1887, 667). A. G. B.

Hydrazines. By C. WILLGERODT (*J. pr. Chem.* [2], **37**, 449—454).—Two symmetrical dinitrophenyl-phenylhydrazines seem to be formed by the action of an alcoholic solution of symmetrical meta-dinitrochlorbenzene on phenylhydrazine; in the cold a solid is formed, but in the warm from the same mixture a syrup was obtained on several occasions. If further researches should prove the existence of the syrupy modification, it must be a geometrical isomeride of the solid. The question will soon be set at rest, as the author has obtained the syrupy compound alone by employing ethereal in place of alcoholic solutions of the reacting substances.

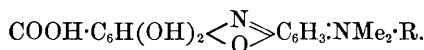
Nitrobromophenyl-phenylhydrazine, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{NH} \cdot \text{NHPh}$ [4 : 1 : 3], is obtained by mixing symmetrical orthodinitrobromobenzene with phenylhydrazine in cold alcoholic solution; it forms red needles melting at 165° . When it is heated in glacial acetic acid, *nitrosobromazobenzene*, $\text{NO} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{N} \cdot \text{NPh}$, is obtained as white needles melting at 124° , and when it is oxidised with mercuric oxide, *nitrobromazobenzene* is produced in red needles melting at 103.5° . A syrup is obtained by the action of symmetrical orthodinitrobromobenzene on phenylhydrazine in cold ethereal solution, which is also converted into nitrosobromazobenzene by glacial acetic acid, and into nitrobromazobenzene by mercuric oxide. The behaviour of tolyl- and other hydrazines, as well as the whole subject, is still undergoing investigation.

A. G. B.

Indamines and Indophenols. By R. NIETZKI and R. OTTO (*Ber.*, **21**, 1736—1745).—Gallocyanin (Koechlin, *Abstr.*, 1883, 796) is very sparingly soluble in water, alcohol, and glacial acetic acid, readily in aniline, with formation of an anilide; alkalis and alkaline carbonates dissolve it readily with reddish colour. It has the composition expressed by the formula $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_5$. The *anilide*, $\text{C}_{27}\text{H}_{21}\text{N}_4\text{O}_4$, already mentioned, crystallises in long needles with a greenish lustre, yields crystalline but unstable salts with acids, and is decomposed by alkalis into gallocyanin and aniline.

The dye known as “prune,” obtained from methyl gallate and nitrosodimethylaniline, has the formula $\text{C}_{15}\text{H}_{12}\text{MeN}_2\text{O}_5$. It is a stronger base than gallocyanin, and does not yield an anilide when crystallised from aniline, but an additive compound, $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_5 \cdot \text{C}_6\text{H}_7\text{N}$.

The constitution of gallocyanin is probably—

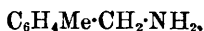


A *diacetyl-derivative*, $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_7$, was prepared, which crystallises in small, greenish needles.

Quinonedichlorimide reacts with β -naphthol in alcoholic solution with formation of a reddish-violet dye, which is readily precipitated as the zincchloride. When this is dissolved in water and treated with nitric acid, the *nitrate*, $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_7 \cdot \text{HNO}_3$, separates. The blue dye prepared by Meldola (*Abstr.*, 1880, 162), by the action of nitrosodimethylaniline on β -naphthol, is without doubt the dimethyl-derivative of this substance, and must therefore have the formula $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}$ (instead of $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}$).

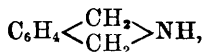
N. H. M.

Phthalimide. By E. BAMBERGER and R. MÜLLER (*Ber.*, **21**, 1888—1892).—When phthalimide in portions of 6 grams is dissolved in 150 grams of amyl alcohol and treated with 12 grams of sodium, a substance, termed by the author *orthotolubenzylamine*,



is obtained as the chief product. This is identical with Strassmann's orthoxylylamine (this vol., p. 474). It boils at 201° under 718 mm. pressure, and at 125° under 105 mm. pressure; it is sparingly soluble in cold water. When exposed to air it solidifies, forming lustrous needles of the carbonate. The *picrate* forms very lustrous, branched needles, which decompose at 205—220° without melting.

A second, more feeble base, probably of the formula



is also formed in the reduction of phthalimide. It is a clear liquid, of an odour resembling that of quinoline and of conine; the *hydrochloride* forms white plates. The *platinochloride* crystallises in lustrous, orange-coloured needles.

N. H. M.

Action of Sulphur on Benzaldehyde. By A. GAZZARRINI (*Chem. Centr.*, 1888, 781—782, from *Atti Acad. Sci. Toscano*, **6**, 64—65).—Sulphur does not readily act on benzaldehyde, for when the two substances are heated together in a sealed tube at 160°, no visible action takes place even after eight hours. On heating the tube at 180° for eight hours, and finally at 190° for 15 hours, the two substances do react. Hydrogen sulphide occurs among the gaseous products. The solid products of the reaction are benzoic acid and a substance containing sulphur, which crystallises in silky, prismatic needles.

All attempts to separate this latter substance from the benzoic acid either by neutralising the benzoic acid with sodium carbonate or barium hydroxide, or by fractional distillation failed, only benzoic acid and a metallic sulphide or hydrogen sulphide being obtained. This substance is easily soluble in ether and undergoes decomposition very easily in air and in contact with water, especially in the warm.

J. P. L.

Combination of Mannitol Anhydride with Benzaldehyde. By J. MEUNIER (*Compt. rend.*, **106**, 1425—1426).—10 grams of mannitol, 20 grams of absolute alcohol, and 5 grams of fused zinc chloride are mixed together, treated with dry hydrogen chloride, and allowed to remain for two days. The liquid portion is then decanted from unaltered mannitol, and mixed with one-fifth the quantity of benzaldehyde. There is a rapid and abundant formation of acicular crystals of the compound $\text{C}_6\text{H}_5\text{O}_2(\text{C}_7\text{H}_5\text{O})_3$. These are washed with water and alcohol and recrystallised from benzene. They are insoluble in water, slightly soluble in alcohol, and much more soluble in boiling benzene, melt at 207° with slight decomposition, and tend to remain in superfusion. The compound is not affected even by boiling alcoholic solutions of the caustic alkalis, but is readily decomposed by acids with liberation of benzaldehyde.

C. H. B.

Action of Chloracetonitrile on Benzene in presence of Aluminium Chloride. By P. GENVRESSE (*Bull. Soc. Chim.*, **49**, 579—581).—The author heated chloracetonitrile (1 mol.) and benzene (3 mols.), together with aluminium chloride ($1\frac{1}{2}$ mols.), for about 12 hours and poured the cold mixture into water. The reaction-product, mixed with the excess of benzene and chloracetonitrile, separated, and was fractioned. Orthotoluic acid, benzoic acid, and orthotolunitrile were isolated from the mixture, but only a small portion of the chloracetonitrile had been acted on. F. S. K.

Methyl Benzoylcyanacetate and Cyanacetophenone. By L. BARTHE (*Compt. rend.*, **106**, 1416—1418).—Benzoic chloride dissolved in ether is added gradually to a well-cooled solution of methylcyanacetate and sodium methoxide in methyl alcohol. The liquid is heated to complete the reaction, and extracted with ether and a solution of sodium carbonate. The aqueous liquid is removed, filtered, neutralised with sulphuric acid, and the precipitate recrystallised from alcohol. *Methyl benzoylcyanacetate* forms long, transparent, prismatic crystals which melt at 74° , and are soluble in ether and alcohol. It gives a red colour with ferric salts, and the alcoholic solution has an acid reaction. The sodium-derivative,



is obtained by dissolving the compound in alcohol, adding sodium carbonate to the hot solution, and allowing the neutral liquid to evaporate spontaneously. It forms hard, white, transparent crystals which decompose at 120 — 125° , and are soluble in water or alcohol. The barium-derivative is obtained in a similar manner, and crystallises with 1 mol. H_2O .

When methyl benzoylcyanacetate is boiled with water, carbonic anhydride is evolved; and when the liquid is cooled, it deposits cyanacetophenone, $\text{CPh}\cdot\text{CH}_2\cdot\text{CN}$, in long, silky, white needles which melt at $81\cdot5^{\circ}$. C. H. B.

Synthesis of Toluoylpropionic Acid. By E. BURCKER (*Bull. Soc. Chim.*, **49**, 448—450).—*Toluoylpropionic acid*, $\text{C}_7\text{H}_7\cdot\text{CO}\cdot\text{C}_2\text{H}_4\cdot\text{COOH}$, is formed by the action of succinic anhydride on toluene in presence of anhydrous aluminium chloride. It crystallises from boiling water in laminæ or slender needles, is readily soluble in ether, alcohol, benzene, chloroform, toluene, and boiling water, but insoluble in cold water; it melts at 120° . When heated slightly above this temperature, it turns red, and retains the colour when cold; at a higher temperature it is decomposed. The *potassium* and *sodium* salts are readily soluble in water. The *barium* salt, $(\text{C}_{11}\text{H}_{11}\text{O}_3)_2\text{Ba} + 4\text{H}_2\text{O}$, is soluble in boiling water, from which it separates in mamelons which lose the whole of their water at 110° . The *silver* salt, $\text{C}_{11}\text{H}_{11}\text{O}_3\text{Ag}$, crystallises in small needles and is insoluble in water. The *cobalt*, *nickel*, and *copper* salts are crystalline. F. S. K.

Dianilidosuccinic Acid. By J. GORODETZKY and C. HELL (*Ber.*, **21**, 1795—1801).—*Ethyl dianilidosuccinate*, $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4$, is prepared by

heating pure ethyl dibromosuccinate with aniline (4 mols.) on a water-bath. The product is extracted with ether, the ether distilled off, and the residue again heated on the water-bath, when a further separation takes place. The crystals are digested with water made slightly acid with hydrochloric acid to remove the aniline salt and recrystallised from alcohol. It forms slender needles of a silky lustre, melts at 150° , dissolves readily in chloroform and hot alcohol, sparingly in ether, benzene, and light petroleum; it also dissolves in strong sulphuric and hydrochloric acids, but is precipitated by water.

Dianilidosuccinic acid, $C_{16}H_{16}N_2O_4$, is obtained by heating the ethyl salt with alcoholic potash at $60-70^{\circ}$; on adding acid to the solution of the potassium salt, it separates as a crystalline precipitate. It is a white, very light powder, almost insoluble in water, light petroleum, and benzene, more soluble in alcohol, warm ether, and chloroform. It melts at 190° with decomposition. The alkali and barium salts are soluble in water; the other salts are almost insoluble. The *sodium salt* crystallises from hot water in lustrous spear-heads; the *potassium salt* is very readily soluble in water, and is precipitated by alcohol in cubes; the *calcium*, *lead*, and *silver salts* are also described.

Ethyl hexabromodianilidosuccinate, $C_2H_2(NH \cdot C_6H_2Br_3)_2(COOEt)_2$, prepared by adding bromine to a solution of ethyl dianilidosuccinate in chloroform, melts at $98-99^{\circ}$ when crystallised from light petroleum, and at $103-104^{\circ}$ when crystallised from alcohol; it is readily soluble in ether, chloroform, benzene, hot light petroleum, and hot alcohol, insoluble in water. The *free acid* is a white, amorphous substance, melts at 230° with decomposition, and is very sparingly soluble in the usual solvents, insoluble in water. The *potassium salt* forms white, lustrous needles rather sparingly soluble in cold water; the *sodium salt* is much more sparingly soluble in water; the *barium*, *silver*, and *ammonium salts* also dissolve very sparingly. The acid as well as its salts are much more stable than dianilidosuccinic acid.

N. H. M.

Chlorides of Bibasic Acids. By V. AUGER (*Bull. Soc. Chim.*, 49, 345-352).—*Succinophenone*, $COPh \cdot C_2H_4 \cdot COPh$, and *diphenylbutyrolactone*, $C_2H_4 \langle \begin{smallmatrix} CPh_2 \\ CO \end{smallmatrix} \rangle O$, are produced when aluminium chloride is added gradually to a mixture of succinic chloride and a large excess of benzene at $25-30^{\circ}$. The reaction product is crystallised from boiling alcohol, when succinophenone separates first in needles; as soon as small leaves begin to deposit, the solution is decanted; the compounds thus separated are recrystallised from alcohol. Succinophenone melts at 134° , and is insoluble in warm concentrated potash.

Diphenylbutyrolactone melts at 90° , and is readily soluble in warm potash; when this solution is acidified, γ -diphenyl- γ -hydroxybutyric acid is precipitated in white flocks which are insoluble in water, but soluble in alcohol. This acid separates from alcohol in large, tabular crystals; when heated at 145° it melts and is reconverted into the lactone with evolution of 1 mol. H_2O . The *barium salt*, $(OH \cdot CPh_2 \cdot C_2H_4 \cdot COO)_2Ba$, crystallises in lustrous, stellate forms which are soluble in water.

From these experiments it follows that succinic chloride is a mixture of the two theoretically possible chlorides.

When succinic chloride is added drop by drop to well-cooled ammonia, succinamide is deposited; the filtered solution is evaporated over sulphuric acid, and the residue extracted with alcohol. A heavy, yellow oil is precipitated when the alcoholic extract is mixed with ether, and this oil solidifies to a granular mass after some weeks. It has the composition $C_2H_4(CONH_2)_2$, is exceedingly hygroscopic, and melts at about 90° . When treated with acids, it yields succinic acid. Its aqueous solution is precipitated by silver nitrate with formation of a silver salt, $C_2H_4 \cdot C_2O_2 \cdot NaAg$, which is almost totally insoluble in water.

Phthalamic acid, $COOH \cdot C_6H_4 \cdot CONH_2$, is prepared by adding hydrochloric acid (1 mol.) to an aqueous solution of ammonium phthalamate; the last named compound is obtained when an ammoniacal solution of phthalic anhydride is crystallised. Phthalamic acid crystallises in small, acute prisms which are sparingly soluble in water. When heated at about 140° it melts, loses water, and is converted into phthalimide. Treated with an excess of hydrochloric acid it is decomposed after some time with formation of phthalic acid. The silver salt is almost totally insoluble in water.

The compound, $C_6H_4 \cdot C_2O_2(NH_2)_2$, is formed, with evolution of heat, when phthalic chloride is added gradually to ammonia. It crystallises from cold alcohol in long, silky needles, and from hot alcohol in long, transparent prisms which are readily soluble in water. When heated, it softens at about 90° , and melts at about 140 – 160° with evolution of ammonia, but solidifies immediately and does not melt again until 232° , the melting point of phthalimide. When silver nitrate is added to an aqueous solution, the salt, $C_6H_4 \cdot C_2O_2 \cdot NaAg$, is precipitated in lustrous scales which are almost totally insoluble in cold water.

The free acid, $C_6H_4 \cdot C_2O_2 \cdot NH$, separates as a curdy precipitate when hydrochloric acid (1 mol.) is added to a dilute solution of the reaction product of phthalic chloride and ammonia. It crystallises from boiling alcohol in long needles which are only sparingly soluble in water. When heated, it melts at about 145° , and is converted into phthalimide. It has an acid reaction, and its aqueous solution decomposes barium carbonate in the cold. If the curdy precipitate mentioned above is crystallised from boiling water, large, transparent needles having the composition $C_{16}H_9O_5N$ are obtained. This compound is very readily soluble in water, to which it imparts an acid reaction. When heated at 145 – 150° it partially melts, but solidifies again, and yields a mixture of phthalic anhydride and phthalimide on further heating.

From these results it follows that phthalic chloride has the asymmetrical formula.

Phthalimide has a distinctly acid reaction, and its boiling aqueous solution decomposes barium carbonate with formation of a barium salt which is soluble in water. When heated with ammonia, it yields ammonium phthalimide in the form of a powder which is reconverted into phthalimide by acids. When the ammoniacal solution is boiled with the precipitate for some time, the latter is completely dissolved,

and an addition of hydrochloric acid does not precipitate phthalimide; the evaporated solution deposits small prisms, which are soluble in water and have an acid reaction.

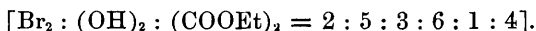
F. S. K.

Constitution of Pyranilpyroic Acid, Pyranilpyroin Lactone, and Anilsuccinic Acid. By A. REISSERT (*Ber.*, **21**, 1942—1947; compare this vol., p. 694).—An answer to Anschütz (*Annalen*, **246**, 115).

Desmotropy. By A. HANTZSCH and F. HERRMANN (*Ber.*, **21**, 1754—1758; compare *Ber.*, **20**, 2800).—Ethyl dichlorohydroquinonedicarboxylate dissolves in benzene, chloroform, and in strong sulphuric acid with intense greenish-yellow coloration, whilst the alcoholic solution, like the substance itself, is colourless. It is shown that the alcoholic solution contains the salt as an alcoholate which separates in large crystals of the formula $C_6H_2O_2Cl_2(COOEt)_2 \cdot 2EtOH$, whilst the salt, when dissolved in solvents which do not combine with it, undergoes the same change as when it is fused, being converted into the coloured modification—ethyl dichloroquinonehydrodicarboxylate.

N. H. M.

Desmotropic Derivatives of Ethyl Succinosuccinate. By M. BÖNIGER (*Ber.*, **21**, 1758—1765).—The ethyl salt, $C_6H_2Br_2O_2(COOEt)_2$, obtained by Herrmann (*Abstr.*, 1886, 1028) by the action of bromine vapour on ethyl quinonedihydroparadicarboxylate, can also be prepared, directly from ethyl succinosuccinate by the action of dry bromine. It is probably ethyl dibromohydroquinonedicarboxylate,



It melts at 157° , and when sublimed in a slow stream of air it undergoes an intramolecular change, and the compound *ethyl dibromokinonehydrodicarboxylate*, $[Br_2 : O_2 : (H, COOEt)_2 = 2 : 5 : 3 : 6 : 1 : 4]$, is obtained in yellow, tabular crystals, which, when kept at the ordinary temperature, recover their original form and colour. The yellow crystals dissolve in benzene, yielding a yellow solution.

When sodium dibromohydroquinonedicarboxylate is dissolved in a little hot water, and carefully acidified, *dibromokinonehydrodicarboxylic acid* separates as a lemon-yellow, microcrystalline powder. This is very unstable, and becomes gradually lighter, until it is finally white. The stable modification, *dibromohydroquinonedicarboxylic acid*, so obtained, is almost insoluble in water, alcohol, and ether.

Ethyl dibromokinonedicarboxylate (Herrmann, *loc. cit.*) melts at 221° . When dissolved in benzene, and treated with ammonia, it is converted into the diamido-derivative.

Ethyl diamidoquinonehydrodicarboxylate, $[O_2 : (NH_2)_2 : (H, COOEt) = 3 : 6 : 2 : 5 : 1 : 4]$, obtained by reducing the above amido-salt suspended in alcohol with tin and hydrochloric acid, forms splendid red needles. It is unstable, and readily becomes changed into ethyl diamidoquinonedicarboxylate. The free acid could not be prepared. The *hydrochloride* crystallises in long, lemon-coloured needles, and is decomposed by water with intense red colour. The *stannochloride*,

$C_{12}H_{16}N_2O_6, SnCl_4 + 2H_2O$, forms long, yellow needles. When the hydrochloride is heated with acetic anhydride, the diacetate of *ethyl diamidohydroquinonedicarboxylate*, $C_6(OH)_2(NHAc)_2(COOEt)_2$, is formed; this crystallises from glacial acetic acid in stellate groups of colourless, lustrous needles, melting at 236° , without decomposition. The *tetracetyl-derivative*, $C_6(OAc)_2(NHAc)_2(COOEt)_2$, obtained by boiling the diacetyl-compound for a long time with an excess of acetic anhydride, is a colourless, microcrystalline substance, melting at 206° . Both acetates are soluble in alkalis.

Dimidoquinonehydrodicarboxylic acid, $[(H,COOH)_2 : (NH)_2 = 1 : 4 : 3 : 6]$, is prepared by saponifying v. Baeyer's so-called ethyl diamidonaphthalate (Abstr., 1886, 445), and forms greenish-yellow, prismatic crystals, almost insoluble in the usual solvents. The *hydrochloride*, $C_8H_8N_2O_4 \cdot 2HCl$, crystallises in colourless plates, which decompose when air-dry, giving off hydrogen chloride. The free acid corresponds with the quinonehydrodicarboxylic acid, whilst in taking up acid it is converted into salts of the colourless modification, diamidoterephthalic acid.

N. H. M.

Isomeride of Orthophenylphthalidecarboxylic Acid. By P. JOUILLARD (*Chem. Centr.*, 1888, 520, from *Arch. Sc. Phys. Nat. Genève*, 19, 121—131).—Phenylacetic acid acts on phthalic anhydride with the formation of benzylidenephthalyl, which reacts with water to form benzylidenephthalylcarboxylic acid. The acid forms an acetoxime melting at 113 — 114° . When oxidised with potassium manganate, *benzilcarboxylic acid*, melting at 137 — 138° , is formed. The methyl salt melts at 117 — 118° , the ethyl salt at 70.5 — 71.5° .

Benzilcarboxylic acid decomposes with potash, like diphtalic acid, phenylphthalidecarboxylic acid being formed; this crystallises with 1 mol. H_2O , which it loses at 100° ; at the same time it undergoes decomposition at this temperature, carbonic anhydride being given off, and the lactone of a benzhydrylcarboxylic acid being formed, which melts at 115° . On oxidation it is converted into orthobenzoylbenzoic acid, melting at 85 — 87° .

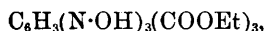
J. P. L.

Ethyl Phloroglucinoltricarboxylate. By O. BALLY (*Ber.*, 21, 1766—1771).—In the preparation of ethyl phloroglucinoltricarboxylate by v. Baeyer's method (Abstr., 1886, 223), an anhydride of the

formula $OH \cdot C \cdot C(COOEt) \cdot C \cdot O$ is formed. This is almost insoluble

in benzene and alcohol, and melts at 168 — 170° . *Ethyl triacetylphloroglucinoltricarboxylate*, $C_6(OAc)_3(COOEt)_3$, prepared by boiling 2 grams of the ethyl salt with 10 grams of acetic anhydride, crystallises from ether or alcohol in needles, melts at 75 — 76° , and is insoluble in cold dilute alkali.

Ethyl triketohexamethylenecarboxylate trioxime,



is obtained by dissolving the ethyl salt in excess of ammonia, and adding hydroxylamine hydrochloride; the product which is a com-

pound of the oxime with ammonia, is treated with dilute acetic acid. It crystallises in groups of slender, reddish needles, which decompose without melting at 169—171°.

Ethyl bromophloroglucinoldicarboxylate, $C_6Br(OH)_3(COOEt)_2$, is formed as a white precipitate when a solution of bromine in carbon bisulphide is slowly added to a solution of the ethyl tricarboxylate in chloroform. It crystallises from alcohol in slender needles melting at 128°.

When an alkaline solution of ethyl phloroglucinoltricarboxylate is treated with chlorine and the product treated with ammonia, trichloracetamide is obtained (compare Hlasiwetz and Habermann; *Annalen*, 175, 260). N. H. M.

Action of Ethyl Sodomalonnate on Resorcinol. By A. MICHAEL (*J. pr. Chem.* [2], 37, 469—471).—The author has previously shown that a fluorescent substance is obtained by the action of ethyl sodomalonnate on alcoholic resorcinol. This substance is better obtained by mixing equivalent proportions of solid sodium ethoxide and resorcinol dissolved in ethyl acetoacetate, and heating for 10 hours in the water-bath in an atmosphere of hydrogen; the resulting mass is then dissolved in water and acidified, whereby the new compound is precipitated. After several recrystallisations from alcohol, it forms slender, white needles, melting with decomposition at 191—191·5°; it is freely soluble in hot alcohol, sparingly so in cold alcohol and hot water, and insoluble in cold water; its alkaline solution is strongly fluorescent. This substance has acid properties, and is not precipitated by carbonic anhydride from its alkaline solution; its formula is $C_{11}H_8O_5$, and as it splits up, at a temperature a little above its melting point, into methylumbelliferone and carbonic anhydride, it is probably β -methylumbelliferonecarboxylic acid; its other properties confirm this supposition.

The formation of this compound by the action of resorcinol on cold alcoholic ethyl sodomalonnate is explained by the intermediate formation of acetone-tricarboxylic acid, which the author has found to occur when an alcoholic solution of ethyl sodomalonnate is allowed to remain in the cold. A. G. B.

Toluidinesulphonic Acids. By J. V. JANOVSKY (*Ber.*, 21, 1802—1805).—Paratoluidineorthosulphonic acid, $[Me : SO_3H : NH_2 = 1 : 2 : 4]$, crystallises in triclinic crystals; $a : b : c = 1.2424 : 1 : s$. The metasilphonic acid crystallises in thin needles, which could not be measured; but their optical properties make it probable that they are rhombic.

Orthotoluidinesulphonic acid (Gerner, *Annalen*, 169, 375) crystallises in large, lustrous, monoclinic prisms; $a : b : c = 0.8889 : 1 : 0.6476$; $\beta = 84^\circ 29'$. Paratoluidineorthosulphonic acid gives no colour reaction with ferric chloride in the cold; when warmed, a bluish Bordeaux-red is produced. Other colour reactions of the three acids are given in a table.

When a trace of lead peroxide is added to cold solutions of paratoluidineortho-, paratoluidinemeta-, and orthotoluidine-sulphonic

acids, yellowish-red, wine-red, and rose colours are produced. The last-mentioned acid yields quinone when oxidised, whilst the other acids do not.

N. H. M.

Indolecarboxylic Acids. By G. CIAMICIAN and C. ZATTI (*Ber.*, **21**, 1929—1935).— α -Indolecarboxylic acid obtained by Fischer from the hydrazone of pyruvic acid, is prepared by fusing methylketole with 10 to 15 parts of caustic alkali. The product is dissolved in water, nearly neutralised with sulphuric acid, filtered from potassium sulphate, concentrated by evaporation, and precipitated with dilute sulphuric acid. It is crystallised from boiling benzene. The *methyl salt*, $C_8NH_5MeO_2$, crystallises in small needles melting at 151—152°. When the carboxylic acid (3 grams) is boiled with acetic anhydride (15 grams), the compound $C_8H_5\begin{smallmatrix} N- \\ \diagup \quad \diagdown \\ CO \end{smallmatrix}$ or $C_8H_5\begin{smallmatrix} N \cdot CO \\ \diagup \quad \diagdown \\ CO \cdot N \end{smallmatrix}C_8H_5$ is formed. This crystallises in almost insoluble, yellow, lustrous needles, which melt at about 312—315°. It is scarcely attacked by boiling with strong aqueous potash, but dissolves readily in hot, alcoholic potash. β -Indolecarboxylic acid, $C_8NH_5O_2$, prepared similarly to the α -compound, crystallises in plates, melts at about 214° with evolution of gas, dissolves sparingly in benzene and in boiling water, more readily in ethyl acetate, ether, and alcohol, and is almost insoluble in light petroleum. The *silver salt*, $C_8NH_5AgO_2$, is a white precipitate. The acid is much less stable than the α -acid, and is decomposed by boiling its aqueous solution. It does not yield a picrate, and gives no precipitate with lead acetate.

In the oxidation of scatole with fused potash, indole and α -indole carboxylic acid are formed as well as the β -carboxylic acid.

N. H. M.

Acetyl-compounds of Methylketole and Scatole. By G. MAGNANINI (*Ber.*, **21**, 1936—1939).—Acetylmethylketole (acetyl- α -methylindole), C_8NH_5MeAc [$Ac : Me = 1' : 2'$] (Jackson, *Abstr.*, 1881, 734, Fischer, *Abstr.*, 1887, 265), is formed in small amount, together with β -acetyl- α -methylindole, when methylketole is boiled with acetic anhydride and anhydrous sodium acetate; when boiled with aqueous potash (sp. gr. 1.22) it decomposes into methylketole and acetic acid. β -Acetylmethylketole is also formed by the action of acetylchloride on methylindole; in presence of zinc chloride a magenta-like dye is produced, which is possibly related to Fischer and Wagner's rosindole (*Abstr.*, 1887, 588). Acetylscatole [$Ac : Me = 2' : 3'$] (this vol., p. 483), dissolves readily in alcohol and acetone, less in ether, and is almost insoluble in cold water; it distils with steam. With hot strong sulphuric acid it gives an intense purple-red solution. The *picrate* crystallises in long, slender, orange-yellow needles. Acetylscatole is not changed by boiling potash; boiling hydrochloric acid decomposes it with formation of free scatole and resin. *Acetylscatoxime*, $C_8NH_5Me \cdot N \cdot OH$, crystallises from dilute alcohol in small needles melting at 119°.

N. H. M.

Conversion of Methylketole into Quinaldine. By G. MAGNANINI (*Ber.*, **21**, 1940—1942; compare *Abstr.*, 1887, 1113).—When

4 grams of bromoquinaldine, from methylketole, is heated with 10 parts of hydriodic acid and some amorphous phosphorus at 180° for 6 to 7 hours, quinaldine is formed, which is purified by means of the picrate. The reaction proves that the bases produced by the action of chloroform and bromoform on methylketole are chloro- and bromoquinaldines, and that they have the constitution $[\text{Me} : \text{Cl or Br} = 2' : 3']$.
N. H. M.

Methylindolecarboxylic Acids. By G. CIAMICIAN and G. MAGNANINI (*Ber.*, **21**, 1925—1929).— *α -Methyl- β -indolecarboxylic(methylketolecarboxylic) acid*, $\text{C}_8\text{NH}_5\text{Me}\cdot\text{COOH}$ $[= 2' : 3']$, is prepared by passing a stream of carbonic anhydride through a mixture of 10 grams of methylketole and 3.6 grams of sodium heated at 230° to 240° for 4 to 5 hours; towards the end, the temperature is raised to 300°. The product is treated with alcohol, dissolved in water, steam distilled, acidified with dilute sulphuric acid, and extracted with ether. The carboxylic acid is crystallised from acetone, dissolved in a mixture of benzene and ethyl acetate, and treated with animal charcoal. The colourless solution is then concentrated and precipitated with light petroleum. It is a white, crystalline powder, melts at 170—172° with evolution of carbonic anhydride, dissolves readily in alcohol, ethyl acetate and acetone, sparingly in benzene and still less in water. It is not stable, and decomposes when the aqueous solution is boiled. The *silver salt* is a white, crystalline precipitate. The aqueous solution of the acid shows the following reactions:—With ferric chloride, a brown coloration and precipitate, with copper sulphate an apple-green precipitate, with lead acetate and with mercuric chloride, white precipitates.

β -Methyl- α -indolecarboxylic (scatolecarboxylic) acid (Wislicenus and Arnold, this vol., p. 361) is obtained in a manner similar to the above compound from 3 grams of scatole and 1 gram of sodium. It crystallises in needles or plates, melts at 165—167° with evolution of carbonic anhydride, dissolves readily in alcohol and ether, less in benzene, and is almost insoluble in light petroleum. It is more stable than the methylketolecarboxylic acid. When heated with sulphuric acid, a splendid purple-red solution is formed.
N. H. M.

3'-Phenylindole. By E. FISCHER and T. SCHMIDT (*Ber.*, **21**, 1811—1812).—*3'-Phenylindole*, $\text{C}_{14}\text{H}_{11}\text{N}$, is obtained when phenylacetaldehyde-phenylhydrazone is treated with hydrochloric acid (compare this vol., p. 698). It crystallises from hot, light petroleum in white leaves, melts at 88—89°, is readily soluble in alcohol, ether, and benzene, rather sparingly soluble in hot, light petroleum and insoluble in water. It distils under the ordinary pressure with only slight decomposition.

The *picrate* crystallises in dark-red needles melting at 107°. When a pine-chip, treated with an alcoholic solution of the indole, is moistened with cold, concentrated hydrochloric acid, it first turns yellow and after some time deep bluish-violet. 3'-Phenylindole yields an oily nitrosamine when treated with nitrous acid, and when heated with zinc chloride at 170° it is converted quantitatively into the isomeric 2'-phenylindole.
F. S. K.

Diphenyl-derivatives. By P. ADAM (*Bull. Soc. Chim.*, **49**, 97—102 (compare *Abstr.*, 1887, 589).—*Methyldiphenyl*, C_6H_4MePh , is a colourless, mobile, refractive liquid which boils at $272-277^\circ$, and dissolves in ordinary organic solvents. It is very stable towards oxidising agents, but chromic acid converts it into metadiphenylcarboxylic acid, melting at $160-161^\circ$. This acid is also formed when the bromine-derivative of methyldiphenyl is boiled with a solution of copper nitrate.

Ethoxymethyldiphenyl, $C_6H_4Ph \cdot CH_2 \cdot OEt$, is prepared by treating methyldiphenyl with bromine and boiling the product with alcoholic potash. It is a colourless, syrupy liquid which is readily soluble in ether and alcohol. The *methyl*-derivative, $C_6H_4Ph \cdot CH_2 \cdot OMe$, is a syrupy liquid with a peculiar smell.

Phenylbenzyl alcohol, $C_6H_4Ph \cdot CH_2 \cdot OH$, obtained by treating the preceding compound with hydrogen iodide, is an odourless, tasteless, thick syrupy liquid which is soluble in chloroform, carbon bisulphide, alcohol, and ether.

Dimethyldiphenyl, $C_{12}H_8Me_2$, is a colourless, mobile liquid which boils at $284-290^\circ$, and is more sparingly soluble in methyl alcohol than the monomethyl-derivative. When oxidised with chromic acid it yields an infusible acid which does not sublime. Paradiphenylbenzene melting at 205° , and the isomeric isodiphenylbenzene melting at 85° , were also isolated from the product obtained by the action of aluminium chloride on a mixture of methyl chloride and diphenyl (*loc. cit.*).

Acetyldiphenyl, $C_6H_4Ph \cdot COMe$, is formed when ethyldiphenyl (*loc. cit.*) is carefully oxidised with chromic acid; it is converted into metadiphenylcarboxylic acid when further oxidised.

Diethyldiphenyl, $C_{12}H_8Et_2$, is a colourless, mobile liquid which boils at $304-310^\circ$. When oxidised with chromic acid, it yields an infusible acid which does not sublime.

Diphenylmethylcarbinol, $C_6H_4Ph \cdot CHMe \cdot OH$, is obtained by acting on acetyldiphenyl with sodium amalgam in alcoholic solution. It melts at $85-86^\circ$ and is very readily soluble in alcohol.

Diphenylphenylenecarboxylic acid (*loc. cit.*) yields benzene and the potassium salt of paradiphenylcarboxylic acid when fused with potash.

F. S. K.

New Method for the Preparation of Tetraphenylethylene.

By P. DE BOISSIEU (*Bull. Soc. Chim.*, **49**, 681—682).—Tetraphenylethylene can be prepared by brominating diphenylmethane and heating the bromodiphenylmethane which is formed to its boiling point; hydrogen bromide is evolved and, after cooling, the crystalline product is purified by distilling and recrystallising from benzene. The yield is 70 to 80 per cent.

F. S. K.

Hydration of Tolane. By A. BÉHAL (*Bull. Soc. Chim.*, **49**, 337—339).—Tolane is converted into desoxybenzoïn when warmed with ordinary sulphuric acid at 60° .

F. S. K.

α -Tetrahydronaphthylamine. By E. BAMBERGER and A. ALTHAUSSE (*Ber.*, **21**, 1786—1795 and 1892—1904).— α -Tetrahydronaphthyl-

amine, $C_{10}H_{11}\cdot NH_2$, is prepared in a manner similar to the β -compound (this vol., p. 599) from 15 grams of α -naphthylamine. The bases, after separation from the hydrochlorides, are distilled in a Glinsky's apparatus. It is a viscous, colourless oil having a slight odour of dimethylaniline, boils at 275° under 712 mm. pressure, dissolves readily in organic solvents, much less in water, and is insoluble in soda. The yield of pure base is 135 grams from 225 grams of commercial α -naphthylamine. It does not react with vegetable dyes. The alcoholic solution reduces silver salts when warmed, gold and platinum salts in the cold. The *hydrochloride* crystallises in tetragonal plates readily soluble in water and alcohol; the *sulphate* with $\frac{1}{2}$ mol. H_2O forms flat needles of a satiny lustre; the *mercurichloride* crystallises in white, lustrous needles readily soluble in hot water; the *oxalate* forms lustrous, white needles which, when heated with water, decompose with formation of an oil having an intense odour of α -naphthylamine; the *picrate*, *nitrate*, and *ferrucyanide* are also described. A carbonate could not be obtained. The *acetyl-derivative*, $C_{10}H_{11}\cdot NHAc$, crystallises in long, matted needles, melts at 158° , and dissolves very readily in the usual organic solvents, rather readily in boiling water.

Phenyl- α -tetrahydronaphthylthiocarbamide, $NHPh\cdot CS\cdot NH\cdot C_{10}H_{11}$, is formed when equimolecular weights of the hydro-base and phenylthiocarbimide are heated for a short time on a water-bath. It crystallises from alcohol in lustrous, thick, concentrically grouped prisms melting at 153° .

Phenyl- α -tetrahydronaphthylcarbamide, $NHPh\cdot CO\cdot NH\cdot C_{10}H_{11}$, prepared from phenyl cyanate, crystallises from benzene in pointed needles melting at 193° ; it is readily soluble in benzene and alcohol.

Di- α -tetrahydronaphthylcarbamide, $CS(NH\cdot C_{10}H_{11})_2$, is formed when a mixture of tetrahydronaphthylamine and carbon bisulphide dissolved in alcohol is boiled for some hours; no reaction takes place in the cold. It crystallises in concentrically grouped, lustrous needles, dissolves readily in alcohol and chloroform, less in ether, and melts at 170° .

α -Tetrahydronaphthol, $C_{10}H_{11}\cdot OH$, is prepared by dissolving α -tetrahydronaphthylamine (1 mol.) in a slight excess of very dilute sulphuric acid, and gradually adding sodium nitrite (1 mol.) to the solution carefully kept cool (below $2-3^\circ$). The crystals of the sulphate which have separated, redissolve, and the whole acquires a yellowish-red colour. After $\frac{1}{2}$ an hour, sulphuric acid (1 : 1) is added, and the liquid boiled until no more nitrogen is evolved; steam is then passed through it, and the distillate, without being filtered, extracted with ether. The residue from the ether is dissolved in soda and precipitated by carbonic anhydride. It melts at $68.5-69^\circ$, boils at $264.5-265^\circ$ under 705 mm. pressure, and dissolves very readily in the usual organic solvents, sparingly in water. It generally separates from the alcoholic solution as an oil which solidifies to large aggregates of thick, lustrous, silvery, rectangular, monoclinic plates. When exposed to air it becomes superficially rose-coloured.

When the acetyl-derivative of α -tetrahydronaphthylamine is treated with bromine, the compound $C_{12}H_{14}NOBr$ is obtained. It forms

clear, lustrous, strongly refractive prisms, melts at 181° , and dissolves readily in alcohol, rather less readily in benzene. It does not give up bromine when treated with alcoholic potash. α -Tetrahydronaphthylamine is oxidised by potassium permanganate to normal adipic acid, $\text{COOH} \cdot [\text{CH}_2]_4 \cdot \text{COOH}$, and oxalic acid. The conversion of α -tetrahydronaphthylamine into naphthylamine is readily effected by means of platinic chloride; oxalic acid seems to produce the same result. The above results make it probable that in α -tetrahydronaphthylamine all four added hydrogen-atoms are present in the benzene-ring to which the amido-group is united. N. H. M.

Acenaphthene and Chlorine. By J. T. KEBLER and T. H. NORTON (*Amer. Chem. J.*, **10**, 217—218).—Chlorine is rapidly absorbed by acenaphthene, much heat being evolved; the final product is a liquid, very viscous when cold, decomposing on distillation and even on keeping; analyses indicate that it possibly may be trichloroacenaphthene. H. B.

Colouring Matter from Anthraquinonedisulphonic Acid and Sodium Nitrite. By J. WALDER (*Chem. Zeit.*, **11**, 1539).—This colouring matter is a brownish-red paste containing 25 per cent. of dry matter; it is not soluble in water or acids, but dissolves in alkalis with a reddish-brown, or when concentrated, a black colour. With cotton mordanted with iron or alumina, or both, it gives tints resembling those of alizarin, which are tolerably fast against soap and chlorine. Its tinctorial power, however, is much less than that of alizarin, and on this account it does not seem suitable for the production of full shades. Its composition is still a matter for conjecture. D. A. L.

Terpinol. By BOUGHARDAT and VOIRY (*Compt. rend.*, **106**, 1359—1361).—Terpilene dihydrochloride was heated with alcoholic potash at 100° for 24 hours and the product washed with water and distilled under reduced pressure. Two-thirds of the product boils at 175 — 180° , and one-third at 215 — 220° .

The first fraction has the composition and properties of citrene. With dry hydrogen chloride at 0° , it yields a dihydrochloride which melts at 47° . This fraction contains no terpane.

The second fraction has a slight odour of terpol, but is more mobile and does not solidify even at a very low temperature; sp. gr. at $0^{\circ} = 0.924$. It is a terpol-derivative of the composition $\text{C}_{10}\text{H}_{16}\text{O}$, and with hydrogen chloride yields ethyl chloride and a dihydrochloride, $\text{C}_{10}\text{H}_{16} \cdot 2\text{HCl}$.

It is evident that the product of the action of alcoholic potash on terpilene dihydrochloride, although seemingly similar to List's terpinol, is in reality very different. C. H. B.

Essence of Eucalyptus Globulus. By R. VOIRY (*Compt. rend.*, **106**, 1419—1421).—The crude essence is a pale-yellow, slightly dextrogyrate liquid with a disagreeable odour; sp. gr. 0.932 . It solidifies at -50° to a mass of crystals which melt at about -10° . This latter property is common to all specimens of the essence of

Eucalyptus globulus and also to the essences of many other species. The first fractions contain water, formic and acetic acids, and butyric and valeric anhydrides. The fraction 158—160 consists of terebenthic hydrocarbon with a dextrorotatory power $[\alpha]_D = +40^\circ$; sp. gr. at $0^\circ = 0.88$. With hydrogen chloride it yields a crystalline monohydrochloride which melts at $126\text{--}128^\circ$ and has a rotatory power $[\alpha]_D = +27^\circ 30'$. The fraction 170—175° consists of eucalyptol, $C_{10}H_{18}O$, which constitutes about two-thirds of the essence. It is purified by crystallisation at a low temperature and forms a colourless, mobile liquid, which has an odour of menthol or camphor and solidifies at 0° and melts at 41° ; sp. gr. = 0.940. It is optically inactive, and with hydrogen chloride yields a hydrochloride, $2C_{10}H_{18}O.HCl$, agreeing in its properties with that obtained by Woelkel from cineol.

Schimmel's method for the extraction of eucalyptol from the hydrochloride does not give a pure product.

When essence of eucalyptus is distilled under reduced pressure it yields a terpinenol which boils at $130\text{--}135^\circ$ under a pressure of 40 mm., and forms a dihydrochloride, $C_{10}H_{16}.2HCl$. The fractions at higher temperatures contain ethereal salts of this terpinenol with acetic, butyric, and valeric acids. The last fractions consist of resins and polymerides of terebenthene. Essence of eucalyptus also contains a sulphur compound which decomposes with evolution of hydrogen sulphide when heated.

C. H. B.

Essence of Cajeput. By R. VOIRY (*Compt. rend.*, **106**, 1538—1540).—Essence of cajeput is a green liquid with a penetrating odour, a column of 10 cm. having a levorotatory power of -2° ; sp. gr. at $0^\circ = 0.934$. It crystallises at -50° , and the crystals melt at -8° .

The fraction at $70\text{--}100^\circ$ contains aldehydes, including butaldehyde and valeraldehyde; the fraction at 155° under ordinary pressure consists of a small quantity of a levogyrate terebenthene which forms a crystalline monohydrochloride with a rotatory power $[\alpha]_D = -4^\circ$. The fraction at 165° contains benzaldehyde.

The greater part of the essence, however, boils at $175\text{--}180^\circ$, and consists of *cajeputol* or cajeput terpane, $C_{10}H_{18}O$, identical with the terpane from essence of eucalyptus.

The fraction at $130\text{--}140^\circ$, under a pressure of 40 mm., has the composition of terpinenol, but will not crystallise, probably owing to the presence of a small quantity of its acetate. If saponified with alcoholic potash at 100° and redistilled, it forms a viscous liquid which boils at $125\text{--}130^\circ$ under a pressure of 40 mm.; sp. gr. at $0^\circ = 0.947$. It is an inactive terpinenol which forms a dihydrochloride, and is identical with the terpinenol described by Bouchardat and Lafont.

The higher fractions contain the acetate of this terpinenol together with small quantities of the butyrate and valerate. Hydrocarbons are also present which boil at 160° in a vacuum.

C. H. B.

Oil of Peppermint. By A. JANDOUS (*Chem. Centr.*, 1888, 581, from *Böhm pharm. Zeit.*, **7**, 71).—In commerce a peppermint oil occurs which is without the usual smell, but which is nevertheless

quite pure. The peppermint oil extracted by the author from some specimens of undoubted *Mentha piperita* had a peculiar smell like balm mint, and quite different from the smell of the ordinary peppermint oil.

Mentha forms hybrids with extraordinary ease, and the smell of the oil appears to change also. J. P. L.

Salts of Camphoric Acid. By I. H. MANNING and G. W. EDWARDS (*Amer. Chem. J.*, 233—235).—*Manganese camphorate*, $\text{MnC}_{10}\text{H}_{14}\text{O}_4$, is obtained by heating a mixed solution of manganous sulphate and potassium camphorate; it is less soluble in hot than in cold water, and is not crystalline. *Chromium camphorate*,



is a heavy precipitate. The basic *ferric salt* is a yellowish precipitate. The *mercuric salt*, $\text{HgC}_{10}\text{H}_{14}\text{O}_4$, is an insoluble, white precipitate. The *aluminium salt*, $\text{Al}_2(\text{C}_{10}\text{H}_{14}\text{O}_4)_3$, is formed by boiling aluminium hydroxide with camphoric acid; it is quite insoluble. The *nickel salt*, $\text{Ni}(\text{C}_{10}\text{H}_{14}\text{O}_4)_2$, is prepared by dissolving nickel hydroxide in the acid and heating, when it separates as a crystalline crust. The *strontium salt*, $\text{SrC}_{10}\text{H}_{14}\text{O}_4 + 6\text{H}_2\text{O}$, is soluble and crystalline.

H. B.

Nitrocamphorates. By P. CAZENEUVE (*Bull. Soc. Chim.*, 49, 92—97; compare Abstr., 1887, 842).—*Sodium nitrocamphorate*, $\text{NO}_2\cdot\text{C}_{10}\text{H}_{14}\cdot\text{ONa}$, prepared by adding sodium carbonate to an alcoholic solution of the zinc salt, crystallises from hot alcohol in large, anhydrous tufts which decompose when heated, are very readily soluble in water and alcohol, but insoluble in ether. Its dextrorotatory power is $[\alpha]_D = +289^\circ$. The *potassium salt*, $\text{NO}_2\cdot\text{C}_{10}\text{H}_{14}\cdot\text{OK}$, forms cauliflower-like masses. The *ammonium salt* is obtained in slightly yellowish, amorphous crusts. The zinc salt crystallises in large, white, efflorescent, hexagonal plates containing 1 mol. of water. It is very sparingly soluble in water and ether, soluble in alcohol, and has a dextrorotatory power $[\alpha]_D = +275^\circ$. The calcium, barium, ferrous, ferric, silver, copper, and lead salts are also described.

Quinine nitrocamphorate, $(\text{NO}_2\cdot\text{C}_{10}\text{H}_{14}\text{O})_2\cdot\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2\cdot\text{H}_2\text{O}$, prepared from the sodium salt and quinine hydrochloride, crystallises in needles which are sparingly soluble in cold water, more readily in hot water, alcohol, and ether. It turns yellow when heated at 127° , and melts at 131° with decomposition. Its dextrorotatory power in a 2.72 per cent. alcoholic solution is $[\alpha]_D = +45.9^\circ$. F. S. K.

Sugars from Hesperidin and Isohesperidin. New Formulæ of Hesperidin and Isohesperidin. By C. TANRET (*Bull. Soc. Chim.*, 49, 20—23).—Hesperidin and isohesperidin, when boiled with dilute sulphuric acid, yield 50 to 55 per cent. of a sugar and 50 to 55 per cent. of hesperitin, melting at 222° with decomposition. The sugar is a mixture of two parts of glucose with one part of isodulcitol. The combined weight of the products was, in every case, greater than that of the glucoside taken, from which it follows that the decomposition takes place with fixation of the elements of

water. From these results the author concludes that the formula of hesperidin is $C_{50}H_{60}O_{27}$, and that of isohesperidin $C_{50}H_{60}O_{27}, 5H_2O$, both of which agree with the results of elementary analysis.

F. S. K.

Vernonin. By E. HECKEL and F. SCHLAGDENHAUFFEN (*Compt. rend.*, 106, 1446—1449).—*Vernonia nigritiana* grows on the West Coast of Africa, where it is known as Batiator or Batjentjor, and is in some repute as a febrifuge. It is a roughly spherical knotted mass of long, greyish-yellow fibres. It contains no emetine and no alkaloïds. If the alcoholic extract is mixed with lime, evaporated to dryness, and extracted with water, the aqueous solution, unlike the original aqueous solution of the root, has no reducing power. If, however, the lime residue is boiled with hydrochloric acid on a water-bath it yields glucose and a resinous substance which is insoluble in water and in dilute acids. The alcoholic extract of the root contains a glucoside which unites with lime to form an insoluble compound.

The glucoside is a slightly hygroscopic, white powder which forms a pale-yellow solution. It is only slightly soluble in ether and chloroform. With sulphuric acid it gives a brown coloration which changes to purple and persists for several hours. The glucoside has the composition $C_{10}H_{24}O_7$, whilst the resinous substance has the composition $C_8H_{10}O_3$, and it follows that when the glucoside undergoes hydrolysis it assimilates 2 mols. H_2O . The resinous compound gives no well-defined colour reactions, except that with sulphuric acid it gives the same coloration as the glucoside.

The glucoside, which the authors name *vernonin*, is the only active principle in the root. When administered by injection it acts like digitalin, strophanthin, and other cardiac poisons, but its activity is only about one-eightieth of that of digitalin.

C. H. B.

Action of Chlorine on Pyridine, Piperidine, and their Derivatives. By O. BALLY (*Ber.*, 21, 1772—1777).—Chlorine acts on pyridine dissolved in chloroform, yielding a white, flaky additive compound, $C_5NH_5Cl_2$, analogous to Hofmann's bromine-derivative (*Abstr.*, 1879, 733). When chlorine is passed through an aqueous solution of pyridine methiodide the compound $C_5NH_5MeICl_2$ is formed, identical with that prepared by Ostermayer (*Abstr.*, 1885, 813); it melts at 90° (not 82°). When boiled with water, it is converted into pyridine methochloride, with liberation of iodine. The platinochloride of the latter compound melts at $205\text{--}207^\circ$ (not 188°).

The ammonium iodides of piperidine and quinoline behave similarly. When the chloriodide-derivative, above described, is treated with chlorine in presence of alkali, *pyridine methochloride iodotrichloride*, $C_5NH_5MeCl_3ICl_3$, is obtained; it forms bright yellow, slender needles melting at $179\text{--}180^\circ$. When dissolved in alcohol, chlorine is eliminated, and the original pyridine methochloride iodochloride (m. p. 90°) is formed.

Chlorine acts on dry piperidine with explosive violence with formation of much soot. When chlorine is passed through piperidine dissolved in water or chloroform, a heavy oil is formed, which sometimes explodes under water, although not dangerously. The new

compound, $C_5NH_{10}Cl$ [$Cl = 1$], is best prepared by mixing concentrated solutions of bleaching powder and pyridine, extracting the oil with ether, drying quickly with potash, and evaporating off the ether in a vacuum. It has a penetrating, unpleasant odour, and when kept for a few hours deposits white needles of piperidine hydrochloride.

Dichlorohydroxyacetylpyperidine, $OH \cdot C_5NH_4Cl_2Ac$ [$Ac : OH : Cl_2 = 1 : 2 : 3 : 5$], is formed when chlorine is passed through cooled acetyl piperidine (b. p. 224°). An oil, probably trichloroacetylpyperidine, is formed as intermediate product; when this begins to solidify the whole is allowed to become warm, is afterwards heated on a water-bath, and is finally poured into water. It crystallises from water in colourless rhombohedra, melts at 122° , dissolves readily in alcohol, benzene, ether, acetone, hot water, and in alkalis, and reduces ammoniacal silver solutions.

N. H. M.

Condensation of Phenylacetaldehyde with Ammonia and Ethyl Acetoacetate. By A. JEAURENAUD (*Ber.*, **21**, 1783—1784).—*Ethyl benzylutidinehydrodicarboxylate*, $CH_2Ph \cdot C_5NH_2Me_2(COOEt)_2$ [$CH_2Ph : Me_2 = 4 : 2 : 6$], is obtained by heating 8 grams of phenylacetaldehyde (prepared by Erlenmeyer and Glaser's method (*Annalen*, **147**, 83, 98, and **195**, 140), 17 grams of ethyl acetoacetate, and 20 grams of 8 per cent. alcoholic ammonia in a reflux apparatus on a water-bath under a pressure of 20 cm. of mercury. It crystallises in needles, melts at 115° , and dissolves readily in alcohol, ether, and benzene. When the alcoholic solution is treated with nitrogen trioxide, ethyl lutidinedicarboxylate and benzoic acid are formed.

N. H. M.

A New Quinolinequinone. By J. MATHÉUS (*Ber.*, **21**, 1886—1888).—*Orthonitrosoparahydroxyquinoline*, $NO \cdot C_9NH_5 \cdot OH$ [$= 1 : 2$], is prepared by gradually adding sodium nitrite (1 mol.) to a cooled solution of parahydroxyquinoline (1 mol.) in dilute hydrochloric acid (2 mols.). After some time, the nitroso-compound is carefully precipitated with ammonia, dried, and crystallised from glacial acetic acid, from which it separates in gold-coloured needles. The yield is almost quantitative. The solutions in soda and in sodium carbonate are green, and deposit the sodium salt in green needles. When reduced with stannous chloride, amidoparahydroxyquinoline is obtained.

Orthonitroparahydroxyquinoline, $NO_2 \cdot C_9NH_5 \cdot OH$, is obtained by treating the nitroso-compound with not too dilute nitric acid. It crystallises from the dilute aqueous solution in groups of slender, pale yellow needles, and from more concentrated solutions in reddish-brown, rhombic plates; it melts at 134° , dissolves readily in hot alcohol and dilute acids, sparingly in cold water, and is insoluble in ether and chloroform. The *hydrochloride* crystallises in slender, white needles readily soluble in cold water; the *potassium* and *sodium salts* form splendid orange-coloured needles and yellowish-brown needles respectively.

Quinolinequinone is prepared from parabenzeneazoparahydroxyquinolinesulphonic acid, or from orthamidoparahydroxyquinoline.

The solution of the latter compound in hydrochloric acid is evaporated down a little, allowed to become cold, treated with dilute sulphuric acid, and then with a slight excess of ferric chloride. The reddish-brown crystals which separate are dried on tiles, and treated with hot water and with barium chloride; on evaporating down the filtered solution, the *hydrochloride* separates in long, reddish-yellow needles. The *sulphate* forms yellow, rhombic plates. The compound is decomposed by soda and by sodium carbonate with brown coloration; with ammonia a green solution is obtained, which quickly becomes blue from above. (Compare this vol., p. 851.) N. H. M.

Action of Sulphur on Quinaldine. By W. V. MILLER (*Ber.*, **21**, 1827—1828).—When sulphur and quinaldine are heated together hydrogen sulphide is evolved, and a series of compounds formed among which is a basic substance free from sulphur. This compound is probably *diquinaldyl*, $C_{20}H_{16}N_2 \cdot H_2O$; it crystallises from hot alcohol in needles, melts at 160 — 162° , and loses water at 110° . The *picrate* and *platinochloride* of this base crystallise in needles. F. S. K.

Quinoline-derivatives. By H. WEIDEL and M. BAMBERGER (*Monatsh.*, **9**, 99—115; compare *Abstr.*, 1887, 847).—When oxygen gas is passed over equal parts of dry quinoline and orthotoluidine hydrochloride, mixed with a small quantity of platinised asbestos, for several hours at 180 — 190° , the temperature being finally raised to 200 — 205° , the mass assumes a reddish colour, and contains paramido-methyl- α -phenylquinoline (pseudoflavaniline), formed by condensation with elimination of hydrogen as water. Pseudoflavaniline may be readily purified after separation from the unattacked toluidine, by alternately dissolving it in dilute hydrochloric acid and precipitating with ammonia. It is isomeric with flavaniline (Fischer, *Sitz. k. bayer. Akad.*, 1885, 333) and crystallises from hot water, which only slightly dissolves it, in flexible hair-like needles melting at 112° and volatilising above that temperature with partial decomposition. The dihydrochloride, $C_{16}H_{14}N_2 \cdot 2HCl$, is obtained by dissolving the base in strong, hydrochloric acid; the solution on cooling deposits long, lustrous needles, rapidly decomposed on heating, and when dissolved in hot water forming the monohydrochloride, $C_{16}H_{14}N_2 \cdot HCl$, crystallising in small, yellow, monoclinic needles. The platinochloride, $C_{16}H_{14}N_2 \cdot H_2PtCl_6$, forms small, pale orange-coloured needles which dissolve in water without decomposition. The acetyl-derivative, $C_{16}H_{13}N_2 \cdot Ac$, crystallises in small scales melting at 176 — 177° (uncorr.).

When treated with nitrous acid and the resulting diazo-compound is decomposed, pseudoflavaniline yields *pseudoflavenol*, $C_{16}H_{12}N \cdot OH$, melting at 195 — 196° (uncorr.). The hydrochloride of this base, $C_{16}H_{13}NO \cdot HCl + 2H_2O$, crystallises from water in pale yellow needles, the platinochloride, $(C_{16}H_{13}NO)_2 \cdot H_2PtCl_6$, is a dull yellow, crystalline powder consisting of minute needles, and the acetyl-derivative, $C_{16}H_{12}NO \cdot Ac$, forms glistening plates melting at 106° . *Nitropseudoflavenol*, $NO_2 \cdot C_{16}H_{12}NO$, crystallises in small, silky needles melting at 160° (uncorr.). *Hydroxypseudoflavenol* forms colourless scales, in-

soluble in water and dilute acids, and melts at 89° . Pseudoflavenol on oxidation with chromic acid yields 2'-quinolinecarboxylic acid (quinaldic acid, m. p. 156.8°), and on distillation with zinc-dust, a new base of the formula $C_{16}H_{11}N$ is obtained.

Metatoluidine hydrochloride, when heated with quinoline in oxygen gas, behaves like orthotoluidine hydrochloride and forms a condensation product; no such compound, however, could be obtained from paratoluidine.

G. T. M.

Phenylquinoline-derivatives. By H. WEIDEL and G. v. GEORGIEVICS (*Monatsh.*, **9**, 138—155; compare Weidel and Bamberger, preceding Abstract).—A gentle stream of oxygen gas is passed over a mixture of parahydroxyquinoline hydrochloride (36 grams), aniline hydrochloride (25 grams), aniline (18 grams), and platinised asbestos (3 grams), at 220° for five or six hours, the temperature finally being raised to 230 — 235 , when no more water and aniline vapours escape; the mixture becomes semi-solid and of a red colour, and contains paramido- α -phenylparahydroxyquinoline, $NH_2 \cdot C_6H_4 \cdot C_9NH_5 \cdot OH$, and amidoparaphenylquinoline, $NH_2 \cdot C_6H_4 \cdot C_9NH_5$. In order to separate these substances the product is dissolved in acidified water, the solution is filtered, treated with excess of alkali, and shaken with ether, which dissolves the amidoparaphenylquinoline and any undecomposed aniline. On passing carbonic anhydride through the aqueous solution, the amidophenylhydroxyquinoline is precipitated.

Amidoparaphenylquinoline is insoluble in water, but dissolves readily in ether, benzene, alcohol, acetone, and chloroform, from which it crystallises in forms belonging to the monoclinic system. It melts at 182° (uncorr.), and can be sublimed without decomposition. The hydrochloride, $C_{15}H_{13}N_2 \cdot HCl + 2H_2O$, crystallises in bright red needles. When oxidised with permanganate in acid solution, the base yields α -hydroxynicotinic acid, hence the aniline-group is attached to the benzene ring of the quinoline molecule.

Paramido- α -phenylparahydroxyquinoline is best purified by repeated crystallisations of its hydrochloride. The base is only slightly soluble in water, ether, alcohol, benzene, and xylene, but dissolves more readily in amyl alcohol, from which it crystallises in small needles melting with decomposition at about 294° . The hydrochloride, $C_{15}H_{13}N_2O \cdot HCl + \frac{1}{2}H_2O$, crystallising in dark red granules, and the sulphate, $(C_{15}H_{12}N_2O)_2 \cdot H_2SO_4 + 1\frac{1}{2}H_2O$, in red needles, are both powerful dyes; the acetyl-derivative, $C_{15}H_{10}NOAc_2$, crystallises from alcohol in almost colourless scales. On treating a solution of the base in hydrochloric acid with potassium nitrite and decomposing the resulting diazo-compound, *parahydroxy- α -phenylparahydroxyquinoline* is formed. It crystallises from alcohol in slender, yellowish-white needles, scarcely soluble in water, and melting at 247° (uncorr.).

The constitution of paramido- α -phenylparahydroxyquinoline is shown by the reduction of the corresponding hydroxy-compound, $(C_{15}H_{11}NO_2)$, with zinc-dust, whereby α -phenylquinoline is formed, and further by the production of parahydroxybenzoic acid, when the hydro-compound, resulting from the action of tin and hydrochloric acid on the hydroxy-compound, is fused with potash.

G. T. M.

Naphthaquinolines. By A. COMBES (*Compt. rend.*, 106, 1533—1538).—*Dimethyl- α -naphthaquinoline*.— α -Naphthylamine and acetylacetone in molecular proportions are heated on a water-bath for a short time, and the viscous liquid thus obtained is heated at 100° for half an hour with excess of concentrated sulphuric acid. The product is poured into a large excess of cold water, in which it dissolves completely, and if this solution is made slightly alkaline with ammonia it deposits long, white crystals, which when dried melt at 44° and boil without decomposition at 360—362°. Dimethyl- α -naphthaquinoline forms well-crystallised salts, the solutions of which show a violet fluorescence. The hydrated platinochloride is a bulky, violet substance, which loses water in a vacuum, and forms a violet-brown, amorphous powder which melts at 260° with decomposition.

Dimethyl- β -naphthaquinoline is obtained in a similar manner from β -naphthylamine. It melts at 66—67°, and boils at 380°, becoming red, but can be obtained colourless by distillation in a vacuum. The platinochloride is greenish-yellow, and decomposes without melting at 220°.

In the preparation of dimethylnaphthaquinoline a golden-yellow product is obtained, insoluble in dilute acids, but soluble in alkalis, forming a colourless solution. Acids precipitate yellow crystals, which are also obtained from the ammoniacal solution by simply boiling it. This compound is the sulphonic acid of the naphthaquinoline, $C_{15}H_{13}SO_3$, and can be obtained directly by the action of the acid on the base. The exact constitution of dimethyl- β -naphthaquinoline was not determined.

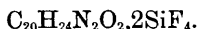
Acetylacetone may be replaced in these reactions by any of its mono-substitution derivatives.

C. H. B.

Action of Silicon Tetrafluoride on Quinine dissolved in Different Liquids. By A. CAVAZZI (*Chem. Centr.*, 1888, 664—665, from *Annal. Chim. Farm.*, 6, 341—346).—Silicon tetrafluoride, when led over dry quinine, has no action whatever. Carbon bisulphide was chosen as a solvent, because Knop and Wolf found that silicon tetrafluoride acted on absolute alcohol, forming tetraethyl silicate and hydrofluosilicic acid, and the author found that it acted on ether after long contact, forming hydrofluosilicic acid and a soluble ethereal silicate.

1 gram of quinine was dissolved in 60 c.c. of carbon bisulphide, and silicon tetrafluoride led over the solution at a distance of 2 cm. from the surface of the solution, which was frequently agitated. The gelatinous precipitate which contained the whole of the quinine was filtered, washed, and dried. It formed a white, amorphous substance, insoluble in carbon bisulphide and ether, but easily soluble in water, which decomposed it with the formation of silicic acid and quinine silicofluoride. This substance melts at a moderately high temperature, and decomposes at higher temperatures with disengagement of silicon tetrafluoride and development of a beautiful carmine-red vapour. Concentrated sulphuric acid decomposes it, with the formation of quinine sulphate and silicon tetrafluoride. In moist air it slowly

becomes sticky, and forms quinine silicofluoride. The author regards it as a mixture of the two compounds $C_{20}H_{24}N_2O_2, SiF_4$ and



If equimolecular weights of quinine and hydrofluosilicic acid are evaporated to dryness at 100° , the normal quinine silicofluoride, $C_{20}H_{24}N_2O_2, H_2SiF_6$, is formed. A better process for obtaining this salt is the following:—Pass silicon tetrafluoride over a solution of quinine in 50 c.c. of absolute alcohol, until the flocculent precipitate which first forms is redissolved, then heat the solution at 40° , and shake, the salt is immediately precipitated as a white, coarse-grained powder. If instead of 50 c.c. of absolute alcohol, 100 c.c. be used, and the solution is not agitated, the normal salt soon separates out in glittering crystals. It is insoluble in ether and carbon bisulphide, soluble in cold absolute alcohol, more readily soluble in boiling alcohol, easily in water. Dilute solutions are strongly fluorescent, and leave on evaporation the unchanged salt. It is hygroscopic, and behaves like the first-mentioned substance both on heating and treatment with sulphuric acid. A watery solution precipitates barium from solutions of its salts, a reaction which might prove useful in the determination of that metal under certain circumstances. The neutral quinine silicofluoride can also be prepared by passing silicon tetrafluoride over an ethereal solution of quinine. J. P. L.

Cinchonibine. By E. JUNGFLISCH and E. LÉGER (*Compt. rend.*, 106, 1410—1411; compare this vol., 380, 507, 729).—*Cinchonibine*, $C_{19}H_{22}N_2O$, is isomeric with cinchonine; it is obtained by dissolving the recrystallised succinate in dilute hydrochloric acid, and precipitating with sodium hydroxide. It forms small, colourless, highly refractive, anhydrous, rhomboidal prisms, which melt at about 259° , and if heated rapidly, sublime without sensible decomposition. It is alkaline to litmus, but not to phenolphthaleïn, and is insoluble in water, dilute alcohol, ether, acetone, or chloroform, but dissolves in hot concentrated alcohol. The rotatory power of a 0.75 per cent. solution in alcohol of 97° at 18° is $+175^\circ.93$; of a 0.5 per cent. solution $+176^\circ.06$. A 1 per cent. aqueous solution, containing two equivalents of hydrochloric acid, has a rotatory power $+220^\circ.53$; with four equivalents of acid $+224^\circ.84$.

The basic salts are slightly alkaline to litmus; the normal salts are acid. The *basic hydrochloride* and *hydrobromide* crystallise in silky needles, very soluble in water; the *platinochloride*, $(C_{19}H_{22}N_2O, PtCl_4)_2 + 3H_2O$, forms small yellow crystals; the *aurochloride* is pale yellow, and only slightly soluble; the *basic thiocyanate*, $C_{19}H_{22}N_2O, CNSH$, forms long, flattened, anhydrous prisms which melt at 203° ; the *basic succinate*, $C_{19}H_{22}N_2O, C_4H_4O_4 + 6H_2O$, is only slightly soluble in cold water, especially in presence of an alkaline succinate, but dissolves readily in water containing succinic acid or in alcohol, and crystallises from either solution in large, hexagonal crystals, or from a boiling aqueous solution in prismatic needles, which melt at 207° when dry; the *basic tartrate* crystallises with 1 mol. H_2O in silky needles, which melt at 214° if dry, and are soluble in water; the *basic oxalate* forms

long, brilliant needles, somewhat soluble in cold water; the *basic chromate* is oily, and only slightly soluble; the *malate* crystallises distinctly; the *phosphate* and *arsenate* are only slightly soluble; the *molybdate*, *picrate*, *benzoate*, and *salicylate* are insoluble and amorphous.

Cinchonidine methiodide, $C_{19}H_{22}N_2O, MeI$, is obtained by the direct union of its constituents at the ordinary temperature, or more readily on heating. It crystallises from boiling water in colourless, anhydrous needles, only slightly soluble in cold, but very soluble in hot water, and soluble in methyl or ethyl alcohol. It melts at 252° . The *dimethiodide* is obtained by using a large excess of methyl iodide, and forms pale-yellow lamellæ, which become red when heated but regain their original colour when cold. They melt at 223° , and are very hygroscopic. The *ethiodide* is obtained in a similar manner, and forms long, colourless, anhydrous needles, which melt with decomposition at 245° , and are slightly soluble in cold water. Crystals which separate from a hot solution are anhydrous, but if formed in a cold solution they contain 1 mol. H_2O . The *diethiodide* crystallises in anhydrous, yellow needles, which melt at 251° . The corresponding bromine compound is obtained by heating its constituents together in presence of alcohol. It forms colourless, anhydrous, crystalline crusts, which melt at 215° , and are very soluble in water, but only slightly soluble in ethyl alcohol. C. H. B.

Piperidine. By E. LELLMAN and W. GELLER (*Ber.*, **21**, 1921—1923).—When piperidine (5 grams) is heated with nitrobenzene (22 grams) at 250 — 260° for four hours it is converted into pyridine.

When piperidine diluted with an equal volume of water is added by drops to a boiling alkaline solution of bleaching powder, and the product steam distilled, the compound $C_5NH_{10}Cl$ (termed by the author piperylene nitrogen chloride) is obtained. This boils at 52° under 25 mm. pressure with slight decomposition, and dissolves readily in alcohol, benzene, ether, and glacial acetic acid. When the solution in much benzene is treated with aluminium chloride, a very small amount of an oily substance, probably tertiary phenylpiperidine, is formed. N. H. M.

Piperylene Nitrogen Chloride. By E. LELLMAN (*Ber.*, **21**, 1924—1925).—Piperylene nitrogen chloride (preceding Abstract) is decomposed by water with formation of much piperidine and a crystalline base, boiling at 150° . When heated with strong hydrochloric acid, chlorine is evolved, and a chloro-derivative is formed, which soon decomposes, and white needles of piperidine hydrochloride gradually separate. N. H. M.

Conversion of Hyoscyamine into Atropine. By E. SCHMIDT (*Ber.*, **21**, 1829).—The author succeeded some time ago in converting hyoscyamine into atropine by heating it for six hours at a temperature above its melting point (compare Will, this vol., p. 855). F. S. K.

Ergotinine and Cornutine. By E. BOMBELON (*Chem. Centr.*, 1888, 472, from *Pharm. Zeit.*, **33**, 109).—Both alkaloids can be

obtained by treating powdered ergot free from fat with alcohol of 95°, in which 50 grams of soda is dissolved, and allowing the mixture to remain for 24 hours. The extract must be again treated with cold alcohol without soda; it contains sphacelinic acid, both alkaloids, some fat, resin, and extractives; it is then acidified with citric acid and distilled to remove the alcohol. The watery solution remaining is filtered (the residue contains the sphacelinic acid), and the filtrate supersaturated with soda and shaken with ether. Ergotinine with some cornutine is dissolved. To separate these alkaloids completely, the dried ergotinine must be again taken up with absolute ether. The alkaloids are only stable when combined with acids; weak watery solutions of the alkaloids quickly decompose. J. P. L.

Hæmatoporphyrin. By M. NENCKI and N. SIEBER (*Monatsh.*, **9**, 115—132).—The authors have previously (*Abstr.*, 1883, 69) ascribed the name hæmatoporphyrin to the substance of the formula $C_{32}H_{34}N_4O_5$, obtained by the action of concentrated sulphuric acid on hæmatin, $C_{32}H_{32}FeN_4O_4$, or hæmin, $C_{32}H_{30}N_4FeO_3$. They now find that when hæmin (or hæmatin, which, however, does not give so good a yield) is treated with a saturated solution of hydrogen bromide in glacial acetic acid, it is readily converted into true hæmatoporphyrin, which shows properties quite different from those previously described. It has the formula $C_{16}H_{18}N_2O_3$, is insoluble in water and dilute acetic acid, is only slightly soluble in ether, amyl alcohol, and chloroform, but is easily dissolved by alcohol, dilute mineral acids, and solutions of the alkalis and alkaline carbonates. The compound is of a reddish colour, is amorphous and very unstable, turning brown and refusing to dissolve in alkalis and hydrochloric acid, after having been heated at 100°. The solution in alcohol or alkalis shows the four absorption-bands described by Hoppe-Seyler and Nobel. The hydrochloride, $C_{16}H_{18}N_2O_3 \cdot HCl$, crystallises in tufts of needles, the sodium salt, $C_{16}H_{17}NaN_2O_3 + H_2O$, in microscopic prisms. The authors have not yet determined whether the compound formed by the action of sulphuric acid on hæmin and hæmatin (*loc. cit.*) is a mixture or is an anhydride of hæmatoporphyrin ($C_{32}H_{34}N_4O_5 = 2C_{16}H_{18}N_2O_3 - H_2O$).

Hæmatoporphyrin has the same empirical formula as bilirubin, which it resembles in many of its properties. When introduced into the living subject, hæmatoporphyrin is partly expelled in the urine, but the greater portion is retained and is probably utilised in the formation of hæmoglobin. G. T. M.

Synthetical Studies on Albuminoids and Proteids. By P. SCHUTZENBERGER (*Compt. rend.*, **106**, 1407—1410).—The author's investigations of the desintegration of albuminoids when boiled with barium hydroxide, show that the products are (1), the products of hydration of urea and oxamide; (2), leucines, and (3), leuceines, the two latter being present in equivalent proportions. In order to effect the synthesis of albuminoids it will be necessary to combine a molecule of a leucine with a molecule of a luceine, with elimination of water, and to then combine this complex group with one or more molecules of urea or oxamide, also with elimination of water.

In order to determine the constitution of the leuceïnes, the zinc salts of the lower leucines, such as glycocine and alanine, were heated at 140—160° in sealed tubes for six hours with zinc oxide and ethylene bromide. The excess of ethylene bromide was poured off, the product dissolved in water and filtered, zinc removed by hydrogen sulphide, barium by sulphuric acid, and bromine by silver carbonate, and the solution was evaporated to dryness in a vacuum. The residue was extracted with alcohol, and the product purified by repeated evaporation and treatment with alcohol. The product is a deliquescent, semi-solid substance, very soluble in alcohol, with all the properties which characterise the leuceïnes obtained from albumin or gelatin. Its solution becomes brown if evaporated in contact with the air. If heated at a high temperature in a current of hydrogen it yields only hydropyrrolic bases, similar to those obtained from leuceïnes. The reactions which take place in the formation of this product may be represented by the equations $\text{NH}_2\cdot\text{CH}_2\cdot\text{COOH} + \text{C}_2\text{H}_4\text{Br}_2 = 2\text{HBr} + \text{C}_4\text{H}_7\text{NO}_2$; $\text{C}_3\text{H}_7\text{NO}_2 + \text{C}_2\text{H}_4\text{Br} = 2\text{HBr}_2 + \text{C}_5\text{H}_9\text{NO}_2$; $2\text{NH}_2\cdot\text{CH}_2\cdot\text{COOH} + 2\text{C}_2\text{H}_4\text{Br}_2 = 4\text{HBr} + \text{C}_8\text{H}_{14}\text{N}_2\text{O}_4$.

C. H. B.

Chemical Nature of the Peptones and the Separation of Albumin from them. By R. PALM (*Zeit. anal. Chem.*, **27**, 359—363).—According to the author's view peptone is a solution of protein in an acid. It can be obtained by the action of lactic acid on the albumin of eggs, milk, or blood, also on gelatin, fibrin, or chondrin. An alcoholic solution of peptone mixed with enough ether gives an oily precipitate containing protein and lactic acid in constant proportions. A peptone solution, neutralised with ammonia, is coagulable by heat, and gives all the reactions of an albumin solution. Mixed with strong alcohol all the albumin is precipitated. This accounts for the fact that peptones show, on analysis, the same composition as the proteins from which they are obtained. Solutions of peptones reduce Fehling's solution. Since cow's milk sometimes contains as much as 1.5 per cent. of peptone, determination of the sugar by that solution gives too high a result.

Peptone solutions are precipitated by potassium xanthate; albumin gives no precipitate until after the addition of an acid.

M. J. S.

Physiological Chemistry.

Acids in Healthy and Disordered Stomachs during a Carbohydrate Diet. By T. ROSENHEIM (*Chem. Centr.*, 1888, 527—528, from *Arch. path. Anat.*, **111**, 414—433).—Ewald and Boas found the following relations in the acids in the gastric juice of a healthy person when a diet of 60 grams of roll and water was taken on an empty stomach. Lactic acid develops very early, and increases for a period of 30 to 40 minutes, during which time hydrochloric acid is

absent, there is then an intermediate period when both acids are present, and a final phase, which lasts to the complete elimination of the stomach contents, when hydrochloric acid only is present. A certain antagonism seems to exist between lactic and hydrochloric acids, which leads to the disappearance of the lactic acid. In opposition, however, to this result, the acidity of the stomach was found to be due to hydrochloric acid alone, which could be detected after 10 minutes, when a 1 to 2 per cent. boiled starch solution was taken.

According to the author's experiments with amylaceous diets, hydrochloric acid appears at a very early stage, it soon reaches a moderately large quantity (above 1 in 1000), and remains essentially the same until the complete passage of the food into the duodenum. Lactic acid is present during all stages of the digestion; the amount which remains fairly constant may, towards the end of the digestion, increase, but it never reaches 1 part in 1000; in every stage of the digestion it is less than the amount of hydrochloric acid.

In pathological conditions, too, the hydrochloric acid can be detected in the very early stages. The amount of hydrochloric acid, both under normal and pathological conditions, is sensibly less when a diet of 25 grams of wheaten starch and 5 grams of sugar or starch only is substituted for the 50 grams of white bread given in the above experiments. In opposition to Ewald and Boas, it is found that the presence of lactic acid in every stage of the digestion, in more or less important quantity, during a purely starch diet, is independent of the amount of hydrochloric acid.

J. P. L.

The Fat Equivalent of Starch (Fattening of Sheep). By T. PFEIFFER and F. LEHMANN (*Bied. Centr.*, 1888, 374—383).—The general results of the experiment made to estimate the fat equivalent of starch, show that Henneberg's factor 2.5 is accurate, and that the nutritive values of saccharose and the other carbohydrates in roots, bran, &c., are to all intents and purposes equal. A table shows the increase of weight of the various parts of the animal as influenced by feeding with sugar and with fat. Sugar appears to increase the consumption of water.

E. W. P.

Formation and Change of Alcohol and Aldehyde in the Organism. By ALBERTONI (*Chem. Centr.*, 1888, 529, from *J. Acad. Belg.*, 1887).—On distillation of fresh or putrid human or animal intestine, a substance was obtained which gave the iodoform reaction, occasionally very markedly, but which could not be an alcohol, as it did not give Vitali's reaction.

Alcohol could only be detected in the breath, urine, and other parts of the body when large doses were given to the animals experimented on; it almost entirely disappears in the organism. Aldehyde, on the other hand, can always be detected in the breath and urine, even when only small quantities have been absorbed, either by the stomach or skin. It is completely excreted by the lungs and kidneys unchanged. If alcohol underwent, according to Liebig's theory, the successive changes into aldehyde, acetic acid, and carbonic anhydride, aldehyde would certainly be found in the breath and

kidneys after alcohol had been taken, which is never the case. The formation of alcohol, either in living or putrefying tissue, is a very rare circumstance. The product mentioned above, which gives the iodoform reaction, is neither alcohol, aldehyde, nor acetone.

J. P. L.

Occurrence of Lactic Acid in Blood and its Formation in the Organism. By M. BERLINERBLAU (*Chem. Centr.*, 1888, 757—758, from *Centr. med. Wiss.*, 1888, 317).—The author has found lactic and sarcolactic acids to be constant constituents of blood: rabbit's blood contained 0.065 to 0.072 per cent., dog's blood, 0.71 per cent., and human venous blood, 0.008 per cent.

Artificial circulation experiments with blood, to which glucose and glycogen had been respectively added, showed that after three hours' circulation a small amount of lactic acid was formed in the case of glucose, and sensibly more with glycogen. Under similar conditions sodium propionate and butyrate were without influence, the greater part of both substances being found afterwards in the blood unchanged.

J. P. L.

Coagulation of the Blood. W. D. HALLIBURTON (*Proc. Roy. Soc.*, 44, 255—268).—The present research was directed to the determination of the nature of the ferment that produces the change of fibrinogen into fibrin. It was found that lymph cells contained the following proteids:—(1.) A mucin-like proteid, similar to that described by Miescher (*Med. Chem. Unters.*, 441). Further experiments showed that this proteid belongs to the class of nucleo-albumins recently described by Hammarsten (this vol., pp. 167, 170). (2.) Two globulins; one which occurs in small quantities enters into the condition of a heat coagulum at about 50°, and the other at 75°. To the latter the name *cell-globulin* is given. (3.) An albumin, to which the provisional name of *cell-albumin* is given. No substance like myosin or fibrin can be obtained from the cells; there is, however, a formation of sarcolactic acid after death, as in muscle; and if the glands are left, especially at the temperature of the body, for some hours after death, a process of self-digestion takes place, the pepsin present in the glands, as it is in most tissues (Brücke), becoming active when the reaction of the tissue becomes acid; under these circumstances there is in addition to the proteids already enumerated a small and varying amount of albumoses and peptones.

In order to ascertain what action, if any, was exerted on the coagulation of the blood by the various proteids that occur in the cells of lymphatic glands, the following experiments were made:—A watery or saline extract of fresh glands had very considerable clotting powers; that is to say, the addition of a few drops of such an extract caused diluted salted plasma to clot in a few minutes, which otherwise did not clot until after the lapse of 12 to 24 hours. The activity of this extract was not altered by heating to 70°; it was therefore independent of the nucleo-albumin which is disintegrated at about 50°, or of the globulin which coagulates at that temperature. Its activity was destroyed, however, if heated above 75°. Extracts of both dried and fresh glands contain a substance which has the

same properties as fibrin ferment, and which, moreover, is rendered inactive at the temperature at which fibrin ferment, as ordinarily prepared from serum, loses its activity.

The next question investigated was whether the ferment action was dependent on, or independent of, the presence of the proteïds of the cells. An extract of the cells was made with sodium sulphate solution, and saturated with ammonium sulphate; the precipitate of the proteïds so produced was filtered off; the proteïd-free filtrate dialysed till free from excess of salt, and it was then found to have no power of hastening coagulation. The precipitate, which contained all the proteïds, was washed with saturated solution of ammonium sulphate, and redissolved by adding distilled water; this solution hastened the coagulation of salted plasma very considerably. This experiment showed either that the ferment was identical with or precipitated with the proteïds in the extract. It was, moreover, destroyed at a temperature at which these proteïds were coagulated, namely, about 75°; there are, however, in the solution, two proteïds which are coagulated at about this temperature, the cell-globulin and the cell-albumin. These were separated by the magnesium sulphate method, and it was found that the globulin and not the albumin has the properties of a fibrin ferment. The question then naturally arose whether this cell-globulin is the same as the substance which has been termed fibrin ferment prepared from serum. A number of experiments were performed with fibrin-ferment prepared in various ways, and the final conclusions drawn are as follows:—

1. Lymph cells yield as one of their disintegration products a globulin which may be called cell-globulin. This has the properties that have hitherto been ascribed to fibrin ferment.

2. Fibrin ferment as extracted from the dried alcoholic precipitate of blood serum is found on concentration to be a globulin with the properties of cell globulin.

3. The fibrin ferment as extracted by saline solutions from "washed blood clot" is a globulin which is also identical with cell globulin.

4. Serum globulin as prepared from hydrocele fluid has no fibrinoplastic properties. It may perhaps better be termed plasma globulin.

5. Serum globulin as prepared from serum has marked fibrinoplastic properties. This is because it consists of plasma globulin, and cell globulin derived from the disintegration of white blood corpuscles, which are in origin lymph cells.

6. The cause of the coagulation of the blood is primarily the disintegration of the white blood corpuscles; they liberate cell globulin which acts as a ferment converting fibrinogen into fibrin. It does not seem to become a constituent part of the fibrin formed.

With regard to Wooldridge's theory of the coagulation of the blood (this vol., p. 305), it is pointed out that lecithin causes a hastening of no other form of plasma but peptone plasma, and it is held that this form of plasma is a very objectionable one to use, both on account of the presence of numerous proteïds foreign to plasma (albumoses and peptones), and on account of alterations in the normal proteïds, as is seen by their heat coagulation temperatures. It is shown that the

elaborate hypothesis of the transference of lecithin from one so-called fibrinogen to another in order to form fibrin, is a pure assumption, and supported by no analytical evidence. The occurrence of a precipitate on cooling plasma (Wooldridge's fibrinogen A) is also considered to be the result of the hetero-albumose present in the commercial peptone used. The mere cooling of a solution of Witte's peptone causes such a precipitate, and this, moreover, consists of rounded granules similar in appearance to blood-tablets. It is urged that the word fibrinogen should be restricted to the substance described by Schmidt and Hammarsten under that name, and that the group of substances obtained by Wooldridge from the tissues (this vol., p. 618), are probably nucleo-albumins, which when injected into the circulation form strings of a mucinoid description in the vessels, which form the starting point for the thrombosis or intravascular coagulation which occurs.

W. D. H.

Malic Acid in Suint. By A. BUISINE and P. BUISINE (*Compt. rend.*, **106**, 1426—1428).—Suint contains malic acid in the form of a potassium salt to the extent of 2·5 per cent. of the solid residue. It also contains succinic acid in similar quantity. The potassium malate is a product of secretion, and is not produced by the fermentation of other constituents of the suint. It is most probable that the malic acid is derived from the food of the sheep, and passes unaltered through the system until it is excreted in the perspiration.

C. H. B.

Animal Melanin. By M. NENCKI and N. SIEBER (*Chem. Centr.*, 1888, 587, from *Arch. expt. Path. Pharm.*, **24**, 17).—Hypomelanin gives *hypomelaninic acid* when melted with potash. The acid is soluble in ammonia, reprecipitated by hydrochloric acid, and contains more carbon and less sulphur than melanin. On purifying the acid, the carbon increases, the sulphur decreases. An attempt to isolate as a chemical product the black pigment of horse's hair failed. An amorphous acid, *sepiaic acid*, was obtained by digesting for a long time the colouring matter from the ink bag of sepia with 15 times its weight of 10 per cent. potash. This acid is soluble in alkaline solutions, and is precipitated from ammoniacal solutions by ammoniacal zinc chloride or copper sulphate. It contains 56·3 per cent. C, 3·6 per cent. H, 12·33 per cent. N, 0·51 per cent. S, and 27·2 per cent. O. The melanin obtained from a melanotic sarcoma of the liver was not identical with phymatorhusin found in previous cases; this is also true of the melanin obtained from sarcomatous inguinal glands and the black pigment deposited in the skin in Addison's disease.

J. P. L.

Buffalos' Milk and Butter. By F. STROHMER (*Chem. Centr.*, 1888, 478, from *Zeit. Nahr. Hygiene*, **2**, 17—19).—In Hungary and Transylvania buffalo's milk is commonly used. A sample analysed by the author gave the amphioteric reaction, had a pleasant taste, but a musk-like smell. Microscopically no difference could be observed between the fat corpuscles of buffalo's milk and ordinary cow's milk; the specific gravity of the milk at 15° was 1·0319, and it contained 81·67 per cent. water and 18·33 per cent. of solid residue; the solids

contained 9.02 per cent. fat, 3.99 per cent. casein, 4.50 per cent. milk-sugar, and 0.77 per cent. ash. The nitrogen was 0.6 per cent., phosphoric acid 0.3 per cent. Another sample, which had become sour before analysis, gave 18.01 per cent. total solids, 8.54 per cent. fat, and 0.62 per cent. nitrogen. The two points in which buffalo's milk, therefore, differs from cow's milk are the high percentage of fat and the musk-like smell.

Butter and cheese made from the milk do not keep well. The fat of buffalos' milk when treated according to Meissl's process was found to contain volatile fatty acids equivalent to 33.6 c.c. of decinormal soda. A salt butter made in Transylvania gave on analysis 17.67 per cent. water, 80.98 per cent. fat, 1.19 per cent. casein and milk-sugar, and 0.16 per cent. ash. The acidity of 100 grams of butter was equal to 23.43 c.c. of normal potash. The butter-fat melts at 31.3°, and congeals at 19.8°. The fatty acids melt at 37.9°. Köttstorfer's equivalent = 222.4 mgrms. of potash. Richert-Meissl's equivalent = 30.4 c.c. of decinormal alkali. The fat does not essentially differ from the fat of ordinary cow's milk either in its chemical or physical properties.

J. P. L.

Excretion of Iron from the Animal Organism and the Amount of this Metal in starving Animals. By S. ZALESKI (*Chem. Centr.*, 1888, 759, from *Arch. Exp. Path. Pharm.*, **23**, 317).—3 c.c. of a solution of sodiotartrate of iron containing 0.0096 gram of iron, was injected into the jugular vein of one of two rabbits of equal weight, fed on the same diet and allowed to fast four days prior to the experiment. Both animals were killed three hours afterwards and the whole circulatory system freed from blood. An analysis of the various organs of both animals showed that in the case of the rabbit which had received the injection of iron the liver was the only organ that contained more iron than the corresponding organs of the control animal. The author draws the conclusion that iron, in contradistinction to other heavy metals, is excreted by the liver and not by the intestine.

J. P. L.

Secretion of Perspiration by the Skin after taking Alcohol. By G. BODLÄNDER (*Chem. Centr.*, 1888, 759—760, from *Zeit. Klin. Med.*, **13**, Heft 5).—An apparatus for readily determining the amount of perspiration from any part of the skin is described. By means of this apparatus the author has found that in the majority of cases alcohol causes a diminution of the amount of perspiration. No ratio, however, between the amount of alcohol taken and the perspiration given off has been observed.

On account of this power of diminishing, in the majority of cases, the amount of perspiration, alcohol may be useful in the case of profuse perspiration of debilitated subjects.

J. P. L.

Toxic Action of Chlorates. By F. MARCHAND (*Chem. Centr.*, 1888, 472—473, from *Arch. Exp. Path. Pharm.*, **22**, 201—232, and **23**, 273—316).—Stockvis has stated that chlorates have no specially toxic properties, sodium chlorate acting like sodium chloride and

potassium chlorate showing only the toxic action of all potash salts; methæmoglobin did not arise in the living blood but only in the dead blood after removal from a vein.

The author points out that Stockvis only experimented on rabbits, the strong alkalinity of whose blood perhaps accounted for the slight action.

When the blood of poisoned animals (dogs) was tested, the methæmoglobin bands were immediately recognisable, so that the author concludes that the living blood undergoes a pathological change. The more rapidly the chlorate is absorbed into the blood, the quicker its action. A quantity of chlorate which when injected into a vein in the course of 73 minutes produced scarcely any result, produced strong symptoms of poisoning when the period of injection was reduced to 30 minutes, and a fatal result when the time was further reduced to 10 minutes.

A similar quantity of chlorate when given by the stomach soon produced changes in the blood and secretion of blood pigment in the urine. The changes in the blood are effected most rapidly by intraperitoneal injection.

Rabbits and guinea-pigs on account of their sensitiveness to irritation of the digestive organs may succumb to gastritis induced by the corrosive action of the chlorate before absorption has taken place.

J. P. L.

Action of Chlorates. By J. CAHN (*Chem. Centr.*, 1888, 473, from *Arch. Exp. Path. Pharm.*, **24**, Heft 3).—Chlorates did not cause the appearance of any methæmoglobin in the blood or urine of rabbits even when hydrochloric acid had been administered to reduce the alkalinity of the blood.

The author corroborates Marchand's results (preceding Abstract), namely, that methæmoglobin very readily occurs when chlorates are administered to dogs.

During marked diuresis more than 3·5 per cent. of sugar was found in the urine. The probable explanation of this is that the chlorate produces changes in the blood similar to those produced in poisoning with amyl nitrite.

J. P. L.

Chemistry of Vegetable Physiology and Agriculture.

Antiseptic Properties of the Naphthols. By J. MAXIMOVITCH (*Compt. rend.*, **106**, 1441—1443).—Numerous experiments show that α -naphthol in the proportion of 2.5 grams and β -naphthol in the proportion of 5.0 grams per litre will kill the microbes in ordinary cultivation liquids and jellies. Their efficiency is greatest in liquids. Different microbes vary considerably in their power of resisting the antiseptic. The microbe which produces a green coloration offers the greatest resistance, and is only killed by 2.5 grams of α -naphthol, or 3.5 grams of β -naphthol per litre. Other patho-

genic microbes require 0.2 to 0.7 gram of α -naphthol and 0.8 to 1.5 gram of β -naphthol per litre. C. H. B.

Origin and Fate of Nitric Acid in Plants. By B. FRANK (*Chem. Centr.*, 1888, 336, from *Ber. deut. bot. Ges.*, 5, 472—487).—Contrary to the general view taken as to the origin of nitric acid in plants, experiments conducted by the author tend to show that nitrates are never formed in the plant, but that the nitric acid must be presented to the plant ready formed. It is then assimilated by the roots, from which it passes to the upper parts by means of the larger cell systems of the stem and leaf ribs. It is these organs which collect the excess of nitrate above that which is required for the healthy growth of the plant. The author points out that in plants such as the ash, in which nitrates are absent from the upper parts, they may yet be detected in the finer rootlets. J. W. L.

Quantitative Estimation of the Heat and Carbonic Anhydride given out by Parts of Plants. By H. RODEWALD (*Bied. Centr.*, 1888, 384—385).—From comparisons of the amount of heat evolved with the carbonic anhydride exhaled by apples, the author comes to the conclusion that the energy set free by the exhalation of gas is in great part converted into heat and external work; this latter may either appear as evaporation of water, or in some cases may be partially utilised in overcoming mechanical obstacles to free growth. E. W. P.

Slow Combustion of Organic Substances. By T. SCHLOESING (*Compt. rend.*, 106, 1293—1296).—The slow combustion of tobacco leaves in presence of air and moisture is at first mainly due to the action of microbes. If the tobacco is sterilised, the quantity of carbonic anhydride formed is very small. At 50° the action of the microbes ceases, and oxidation, which takes place above this temperature, is the result of purely chemical changes. C. H. B.

Atmospheric Nitrogen and its Relations to Vegetation. By E. CHEVREUL (*Compt. rend.*, 106, 1460—1461).—In 1854 a commission, consisting of Dumas, Regnault, Decaisne, Peligot, and Chevreul confirmed a statement by G. Ville to the effect that living plants absorb nitrogen directly from the atmosphere. All subsequent researches, including those of Gautier and Drouin (this vol., pp. 746, 871), afford further confirmation of this conclusion. C. H. B.

Assimilation of Nitrogen by Plants. By WILFARTH (*Ann. Agronom.*, 14, 231—233).—The experiments now reported completely confirm the conclusions arrived at by the author and Hellriegel last year (this vol., p. 742). Oats, buckwheat, colza, peas, sainfoin, and lupins were cultivated in pure sand free from nitrogen. The necessary minerals having been added to this sterile soil, the plants grew normally until the nitrogen stored in the seed was used up. A little garden soil was now rubbed up with water, allowed to subside, and the turbid liquid added to the sterile soil. Each pot contained 4 kilos. sand, and received a quantity of liquid containing 0.3 to 0.7

mgm. of nitrogen. After this addition, the oats, colza, and buckwheat remained undeveloped, but the peas, sainfoin, and lupins rapidly became deep green, and continued to grow vigorously to maturity. The same turbid liquid sterilised by heat had no effect in causing the growth of the leguminous plants. The soil from which the liquid is prepared is a matter of importance. Any soil will answer in the case of peas, but lupins and sainfoin require a soil in which the same plants have been previously grown. 178 experimental pots of plants were grown, and the conclusion is that the papilionaceous plants employed are able to obtain their nitrogen from the atmosphere. The following experiment is cited to prove that the combined nitrogen of the air is not the source of supply:—4 kilos. of the calcined sand, with the requisite minerals, but without nitrogen, were placed in a large flask, and sown with one seed each of oats, buckwheat, and peas. A little soil water was then added, and the flask hermetically sealed, the requisite carbonic anhydride being supplied to the enclosed atmosphere at intervals. The result was the same as with the cultivations in free air; the oat and buckwheat seeds grew only until the nitrogen contained in them was exhausted, whilst the pea grew and furnished 6.55 grams of dry matter containing 0.137 gram nitrogen. Lupins show the absorption of nitrogen better than the other plants. In four experiments when soil water was added to the sand, the total dry weight of crop was 217.28 grams, containing 4.786 grams nitrogen; in four similar experiments without the soil water the total dry weight of crop was only 3.660 grams, containing nitrogen 0.0547 grams.

Whilst it is certain that without soil water (or when this is sterilised) none of the characteristic tubercles will grow on the roots of the papilionaceous plants, and also that they are developed when the soil water is supplied, it cannot yet be asserted that the power of absorbing free nitrogen is dependent on the growth of these tubercles. An editorial note adds that these tubercles can easily be found on the roots of clover, some being as large as a pin's head, and that when bruised in a drop of water, numbers of animated bacteria become visible under the microscope.

J. M. H. M.

Liberation of Silver by Living Cells, and its supposed Connection with Hydrogen Peroxide. By T. BOKORNY (*Ber.*, **21**, 1848—1850).—The agent in living cells which causes the liberation of silver cannot be hydrogen peroxide, as is stated by Wurster, for the following reasons:—It is destroyed by very dilute acids, precipitated by ammonia, gives the reactions for albumin, cannot be extracted, does not give a blue coloration with starch and potassium iodide, does not react with ferrous sulphate and tannin, and is not injurious to living cells even in large quantities.

F. S. K.

Accumulation and Consumption of Glycogen in Fungi. By L. ERRERA (*Chem. Centr.*, 1888, 252, from *Ber. deut. bot. Ges.*, **5**, 74—76).—The author has satisfied himself that a large number of fungi contain glycogen, the only species in which he could not detect its presence being some of the *Uredineæ*. The author also notices a

complete analogy existing between the deportment of the glycogen of the fungi and the starch of the higher orders of plant life; this being especially noticeable in the *Phallus impudicus*. J. W. L.

Formation of Glycogen in Beer Yeast. By E. LAURENT (*Chem. Centr.*, 1888, 252, from *Ber. deut. bot. Ges.*, 5, 76—78).—By cultivating yeast in gelatin, the author succeeded in bringing about an accumulation of glycogen by several species of *Ustilagineæ*. The presence of carbohydrates, egg albumin, and many other substances would seem to promote its formation. J. W. L.

Formation of Calcium Oxalate in Leaves. By A. F. W. SCHIMPER (*Ann. Agronom.*, 14, 175—187, from *Bot. Zeit.*, 1888, Nos. 5—10).—Calcium oxalate is very generally found in leaves, although it seems to be wanting in certain families of plants, such as mosses and most ferns and grasses. In order to observe the distribution of this substance in entire leaves or parts of leaves, the author deprives them of their chlorophyll and intercellular air by alcohol, and then places them for several hours in a solution of 8 parts of chloral hydrate in 5 parts of water. This renders them quite transparent, and the crystals of oxalate may be readily seen on examining them under the microscope with the intervention of Nicol's prisms. Working in this way, the author finds that the *raphides*, or clusters of needles of calcium oxalate, which are only developed in certain plants, are formed while the leaves are very young, and do not increase as the leaf grows. It is quite otherwise with the ordinary crystals of calcium oxalate which are found in the great majority of plants. These are very slightly developed in the young leaves, whereas the old ones are very rich in them. Leaves in full daylight contain more oxalate than those in shade. If any particular leaf is shaded, the oxalate contained will not increase in amount, although it does in neighbouring leaves exposed to the light. A seedling grown in the dark contains very minute crystals of oxalate; these rapidly increase when the plant is brought into the light. The oxalate thus formed is called by the author secondary oxalate; the *raphides* formed in young shoots of certain plants are called primary oxalate; and there appears to be also a tertiary deposit rapidly formed in autumn in old leaves before their fall.

In the case of variegated plants or leaves, the white portions are found to be almost destitute of secondary oxalate, whilst the green portions contain the normal quantity; petals and other portions destitute of chlorophyll are equally destitute of secondary oxalate. A shoot of *Pelargonium zonale* grown for a month in air deprived of carbonic anhydride developed many leaves of the usual size, but delicate, and showing under the microscope no starch granules, but an abundant crop of oxalate crystals. The formation of secondary oxalate therefore appears to depend on the presence of light and chlorophyll, but to be independent of assimilation; it is greatly promoted by free transpiration. The crystals of oxalate once formed are not stationary, but generally redissolve and migrate as a useless bye product to cells other than those in which they are formed. Thus the oxalate

is generally formed in the assimilating cells, and then migrates to the cells disposed along the veins of the leaves, which are so frequently found filled with crystals. A further migration from the leaf towards the stem seems probable. The formation of the tertiary oxalate deposit has been explained physiologically by the observation of Berthelot and André, that the young leaves contain as much oxalic acid as the old leaves, but that in the former it is present chiefly as potassium oxalate, and in the latter as calcium oxalate, that is, when the activity of the leaf ceases, the oxalic acid is fixed by lime, and the potash liberated to migrate to the still living shoots and leaves.

In order to arrive at the physiological meaning of the secondary deposit of calcium oxalate, the author has endeavoured first to solve the problem why lime is an essential constituent of plants. Various plants, among them *Tradescantia selloi*, were grown in a normal nutritive solution, and in the same solution deprived in succession of calcium, potassium, and magnesium salts, also in solutions containing these metals in the forms of nitrate, sulphate, and phosphate respectively. The development of the *Tradescantia* was normal in all the solutions for the first three weeks, and continued to be so in the complete solution. In the solution without lime, the leaves successively became smaller and smaller, brown and dead in patches, and the buds at last dried up. Under the microscope, the assimilating cells of the leaves were seen to be surcharged with starch, so that assimilation was not prevented. The conducting cells were empty of starch, and the raphides of oxalate, formed at first in the youngest shoots, had disappeared. In the solutions without potassium and magnesium salts the old leaves died, but new shoots and leaves continued to be formed. Under the microscope the leaves were seen to be completely deprived of starch and glucose, so that assimilation had ceased, although the migration of carbohydrates continued until new shoots were formed, the plants eventually dying of exhaustion just as if cultivated in air deprived of carbonic anhydride. The addition of a little potash salt caused assimilation to recommence. The cells of the plant grown in the complete solution showed abundance of raphides and of secondary crystalline deposits of calcium oxalate, and when lime was added to the solution hitherto deprived of it, the plant grown in this solution also began to form these crystals after eight or nine days. It follows from this and other experiments that lime is essential to the migration of carbohydrates, although not to their assimilation, and that, having assisted this migration, perhaps by combining with the soluble carbohydrate, it is afterwards converted into oxalate and thrown out of solution. Secondary deposits of calcium oxalate are formed, whether the calcium be supplied as nitrate, phosphate, or sulphate. By a series of microchemical observations the author shows that these salts enter the leaves unaltered, and are often stored up, especially in the hairs. In the leaves, the nitrogen, phosphorus, and sulphur are assimilated, and the lime removed as secondary oxalate. Even detached leaves (etiolated) will absorb the above-mentioned salts from nutrient solutions and live for several weeks, becoming healthy and increasing in size, and it is easy by microchemical means to follow the disappearance of the nitrate reaction (diphenylamine) and the corresponding

decomposition of crystals of calcium oxalate. This decomposition of nitrates takes place only in light and in green cells; probably the assimilation of sulphur and of phosphorus is dependent on the same conditions.

J. M. H. M.

Vanillin in the Seeds of *Lupinus albus*. By G. CAMPANI and S. GRIMALDI (*Chem. Centr.*, 1888, 377, from *Boll. R. Accad. dei Fisiocritici in Siena*, 5).—By distilling the lupine seeds six times with steam and evaporating the distillate to one-tenth of its original volume, a liquid is obtained which smells of vanillin, and turns litmus-paper very gradually red, eventually bleaching it. By extracting this liquid with ether, vanillin is obtained and was purified by recrystallising it from water after having boiled it with animal charcoal. Its melting point (81°) and its reactions proved its identity.

J. W. L.

Presence of Albumin in Cell-fluid. By O. LOEW and T. BOKORNY (*Chem. Centr.*, 1888, 252—253, from *Bot. Zeit.*, 1887, 849—857).—The authors find active albumin in the cell fluid of a number of spirogyra in which it is dissolved. By the action of bases it is precipitated in a granular condition. It reduces alkaline silver solution and with many reagents behaves like egg-albumin. Since the threads of protoplasm consist of active albumin it appears in this precipitated form in them also.

J. W. L.

Morphological and Chemical Composition of Protoplasm. By F. SCHWARTZ (*Ann. Agronom.*, 14, 229—231).—In the long memoir of which this is an abstract, the author elucidates the chemical properties of the substances which can be distinguished morphologically in the protoplasmic body, and describes microchemical reactions by which they can be identified.

Cell-sap and protoplasm.—The cell-sap is sometimes acid, sometimes alkaline. Sometimes it naturally contains a substance sensitive to change of reaction, and therefore serving as indicator; when this is not the case the substance is placed in a solution of red cabbage which is then traversed by an electric current. Under this influence the cabbage solution penetrates the protoplasm and shows its reaction, as well as that of the cell-sap. Protoplasm is never acid, most frequently it is distinctly alkaline. The chromatophores, microsomes, and in some cases the proteic granules, show the same reaction. Probably the alkalinity is due to alkaline phosphates.

Chloroplastides.—The plasmatic substratum of the chlorophyll grains consists of two substances, *chloroplastin* and *metaxin*, the first forming sinuous fibrils, sometimes uniformly green, sometimes charged with little spherules more deeply-coloured. Between the fibrils is the colourless metaxin, hardly visible in the intact chloroplastides. When the chlorophyll granules are treated with water, the chloroplastin is not affected, the metaxin first swells and then dissolves. It is the latter substance which causes the formation of vacuoles in grains of altered chlorophyll.

Nucleus.—Five different substances are contained in the nucleus, two of them, *chromatin* and *linin*, belonging to the framework, the

first forming the microsomes, the second the nucleohyaloplasma of Strasburger.

The nucleole consists of *pyrenin*, which is quite distinct from chromatin. The substance constituting the membrane of the nucleus and resembling pyrenin in most of its reactions, receives the name of *amphipyrenin*. The liquid contents of the nucleus, or nucleochyme of Strasburger, is similar to linin, and is called paralinin. Cytoplasma, or general plasma of the cell, presents very rarely a reticulated or fibrillar structure. It is essentially formed of *cytoplastin*, the only constant proteic substance of protoplasm, which furnishes equally the internal and external membrane of the protoplasmic body. Then come the substances dissolved in the cell-cap or those forming the microsomes suspended in the cytoplastin.

Chloroplastin and cytoplastin are insoluble in concentrated potassium hydrate and in sodium chloride (1 : 10), in which the nucleus dissolves completely. They resist the action of trypsin and pepsin, whilst the substances of the nucleus are digested, pyrenin with difficulty. In hydrochloric acid (1 : 100) chloroplastin swells strongly, cytoplastin is precipitated; in disodium phosphate (5 : 100) the former is insoluble, the latter swells and dissolves. Chromatin and pyrenin fix colouring matters strongly. Pyrenin is insoluble in sodium chloride (20 : 100), saturated solution of magnesium sulphate, acid potassium phosphate (1.5 : 100), potassium ferrocyanide acidified with acetic acid, and copper sulphate. These reagents dissolve chromatin. Chromatin is insoluble and pyrenin soluble (after swelling) in acetic acid (3 : 100) and hydrochloric acid (1 : 100). Amphipyrenin does not fix colouring matters, dissolves less easily than pyrenin in sodium chloride (10 : 100), and more easily in potassium hydroxide (0.1 : 100). Linin and paralinin swell strongly in sodium chloride (20 : 100), lime-water, strong potassium dichromate, and often in water only, and in sodium phosphate (1 : 100), media in which amphipyrenin is insoluble. Solution of magnesium sulphate causes paralinin to swell and does not alter linin; pepsin digests paralinin but not linin. Metaxin, unlike the plastins, is digested by pepsin and trypsin, and is distinguished from the substances of the nucleus by its solubility (after swelling) in hydrochloric acid (0.1 : 100).
J. M. H. M.

Constituents of Calamus Root. By H. THOMS (*Ber.*, 21, 1912—1920).—Calamus root was extracted with light petroleum to remove the oil and then treated with alcohol which extracted a sugar and tannic acid. The root, after this treatment, has no odour, is no longer bitter and has a woody taste. If it is now treated with water an extract is obtained containing potassium and sodium sulphates, an acid salt of tartaric acid, and dextrin.

The sugar of calamus root is dextrose.

Acorin forms a thick, honey-coloured substance of an aromatic odour and bitter taste; it contains no nitrogen and is neutral to litmus. When treated with dilute acid it is decomposed into an ethereal oil, a resin acid, and what is probably a sugar.

When a calamus extract is heated with alkali, trimethylamine is formed (compare Geuther, *Abstr.*, 1887, 972).
N. H. M.

Influence of Sterilisation of Soil on the Growth of Plants.—By TSCHIRCH (*Ann. Agronom.*, **14**, 233—234).—The roots of the beech tree are always enveloped in a layer formed by the interlacing hyphæ of a fungus. If comparative cultivations be made in ordinary forest soil and in the same soil sterilised, it is easily seen that sterilisation has a noxious influence. 10 out of 15 plants died when so treated, whilst all the 15 planted in the unsterilised soil grew and flourished and their roots became covered with the fungus. The author contrasts this with ordinary agricultural crops which do not live in symbiosis with a fungus, and which flourish better in sterilised soil than in soil containing micro-organisms. He asserts that this is true of lupins also, and hence that the root tubercles cannot be of importance to this plant when growing in ordinary arable soil. It does not precisely follow from this that Hellriegel's view is incorrect, since his experiments were made in a soil free from nitrogen, whilst the author's were made in ordinary soil, perhaps containing abundance of ready-formed nitrate. It is still possible, therefore, that these tubercles play an important part in the assimilation of atmospheric nitrogen by the leguminosæ. J. M. H. M.

Absorption Compounds and the Absorptive Power of the Soil. By J. M. VAN BEMMELN (*Landw. Versuchs-Stat.*, **35**, 69—136).—The author first gives an account of the results of his own investigations and those of other observers on the absorptive power of colloid substances for acids, bases, and salts. He studied particularly the gelatinous hydrates of the dioxides of silicon, tin, and manganese, and of some other oxides. These gelatinous hydrates, for which he adopts Graham's name—"hydrogel," when obtained free from apparent moisture, still retain an amount of water varying with the conditions under which they have been dried and which does not correspond with any definite chemical formula. Hydrogels can form absorption-compounds with gases and liquids, and can also, by absorption, remove acids, bases, salts, &c., from solutions with which they are brought into contact. The formation of these absorption-compounds must be ascribed to something more than adhesion, although they cannot be considered as ordinary chemical compounds. When a hydrogel is brought into contact with a solution, the dissolved substance is absorbed by the hydrogel until a state of equilibrium is reached, the tendency of the hydrogel to absorb more of the substance being counterbalanced by the tendency of the solvent to remove the substance from the hydrogel. This state of equilibrium will be altered if the conditions change; such as the temperature, the strength and relative amount of the solution.

The principal phenomena of absorption are as follows :—

1. When a quantity of an absorption-compound gains or loses some of the absorbed substance, in all probability every particle becomes equally richer or equally poorer in the absorbed substance. In this respect such compounds differ from chemical compounds, for when these suffer partial dissociation a certain number of the molecules are completely decomposed and the rest remain intact.

2. The absorptive power is not constant, but varies as absorption

goes on; the attraction for the first portions absorbed is strong and the absorption goes on rapidly; but as more and more is absorbed the tendency to absorb more becomes weaker and absorption takes place more slowly. Conversely, in removing absorbed substances, the first portions are given up readily, and the last portions are retained much more obstinately.

3. The mode of formation and also the drying, warming, &c., of colloid substances cause an alteration in them and change their absorptive power.

4. Hydrogels may change into ordinary chemical hydrates, acquiring a definite composition, and sometimes a crystalline form; but in doing so they lose their power of forming absorption-compounds. The formation of a colloid compound is accompanied by the evolution of considerably less heat than the formation of the corresponding crystalline compound.

5. Temperature affects the absorptive power. Increase of temperature sets free a certain quantity of water from the hydrogel, and also increases the solvent action of the water or the substance absorbed, consequently it causes a diminution in the amount absorbed.

6. Every hydrogel has its own specific absorptive power for each acid, base, and salt. One hydrogel may absorb acids more powerfully than it does other substances, another bases, and a third salts. In general absorption is strongest when under other circumstances the hydrogel and the absorbed substance can combine chemically; for instance, stannic acid absorbs much sulphuric acid, and still more potash.

The substance absorbed may be merely proportionally divided between the water of the hydrogel and the water of the solution, as is the case when potassium chloride is absorbed by the hydrogel of silica; or else a larger proportion than this may be absorbed by the hydrogel, for instance, on separating the hydrogel of metastannic acid from a dilute potash solution, the filtrate is nearly free from potash. The absorption may even cause decomposition of the substance in solution; thus the hydrogel of silica removes some potash from potassium carbonate or some soda from disodium phosphate, leaving a corresponding amount of potassium bicarbonate or monosodium phosphate in solution; also on shaking up the same hydrogel with calcium carbonate and potassium chloride, there is an absorption of lime and potash, corresponding amounts of calcium chloride and calcium bicarbonate being left in the solution, and some potassium chloride is also absorbed.

7. Its condition and its weight being given, the temperature also being given and remaining constant, and the hydrogel not being soluble in the liquid, then the amount of a particular substance absorbed by it varies with the state of concentration and with the amount of the solution. A state of equilibrium is arrived at between the absorptive action of the hydrogel on the one hand and the opposing action of the water on the other; if, however, chemical decomposition of the substance occurs, then the attraction of chemical combination takes a part in producing the equilibrium.

The stronger the solution is the more of the substance is absorbed,

but in a decreasing proportion, and the limit is reached when after the equilibrium point has been attained, the liquid is in a state of saturation.

However much the quantity and however much the state of concentration of the solution may vary in different experiments, yet as soon as equilibrium is reached, according as the final strength of the solution in one experiment is greater or less than in another experiment, then is the amount absorbed also greater or less; and, further, if the final strengths of the solutions are the same in two experiments then also the amounts absorbed are the same; and, conversely, if the amounts absorbed in two experiments are the same, then also are the final strengths of the solutions the same.

Hence a curve can be constructed for a particular hydrogel and a particular substance representing the relation between the amount of substance absorbed and the final strength of the solution.

The author discusses the question whether a mathematical expression can be given for the formation of absorption-compounds. In the case of dilute solutions and provided the absorptive power of the colloid is weak, as is the case with silicic acid and with soil acting on saline solutions, the curve is nearly a straight line, and an expression can be given which is approximately correct. But in other cases no satisfactory formula can as yet be found.

8. One crystalloid absorbed by a hydrogel can be replaced by others. If a hydrogel which has absorbed a substance A be placed in a solution of another substance B, then the solvent will dissolve out some of A, and at the same time the hydrogel will absorb some of B until equilibrium is attained in each case. No true substitution has here taken place. As long as the absorbed quantities are small A and B are absorbed without mutually influencing one another to a noticeable extent; but if the quantity of A is large it may happen that not only does loss of A happen as above, but there may also be a further loss of A owing to its replacement by B, for since A is largely absorbed, part of it is not strongly fixed by the hydrogel, and this part may be replaced by a part of B which the hydrogel fixes the more strongly the smaller the total quantity absorbed of B is. This is a true substitution. By repeatedly treating the hydrogel which has absorbed A with solutions of B, A can be entirely replaced by B. If chemical action occurs between A and B the phenomena are more complicated.

If absorption occurs by chemical substitution, for instance, when the colloid silicates of the soil absorb potash from a potassium chloride solution, in exchange for lime, then the law given under (7) holds good, namely, that a relation exists between the amount absorbed and the final strength of the solution, whatever the proportions and strengths at starting were, and that thus, other things being the same, the absorption depends only on the final strength of the solution.

The author next treats of the absorptive power of the soil. This is chiefly due to the fine particles, and these are mainly composed of colloid substances. The colloid components of the soil are (1) the substances classed as humus; (2) ferric and ferrous hydrates; (3) silicic acid; (4) the amorphous silicates produced by weathering and resembling zeolites.

All attempts that have been made to isolate individual members of the humus-group and assign formulæ to them have failed, for they have been formed from colloids and are of a colloid nature themselves. Soluble humus substances form absorption-compounds with acids and salts, but most easily with bases, hence they were termed acids. The soluble humus acids, in the stage of the so-called crenic and apocrenic acids, can form soluble complex compounds with ammonia, with alkalis, and also with different insoluble bases such as lime, magnesia, ferrous and ferric oxides, &c. This is how it is that brown peat-water in nature contains traces of iron, and that the hydrochloric acid extract of a clayey peat soil (free from excess of hydrochloric acid) often gives no precipitate of ferric or aluminium hydrates on the addition of ammonia.

Humus as it exists in the soil contains ammonia, alkalis, alkaline earths, and ferrous oxide; if this humus is treated with solutions of salts, absorption by exchange of bases will take place; thus on treatment with potassium chloride solution, potash will be absorbed, and lime and magnesia will go into solution. By extracting humus with dilute acid, the bases are removed and this kind of absorptive power is reduced to a minimum.

Peat humus has a strong absorptive power for alkalis, and especially for ammonia. When peat humus is treated with solution of a caustic alkali, part is dissolved, but the undissolved part absorbs much alkali. This kind of absorptive power is not lost after extraction with hydrochloric acid. Humus also removes alkalis from solutions of their salts with feeble acids. When humus is treated with a phosphate of an alkali the alkali is absorbed, turning out some lime and magnesia which precipitate some phosphoric acid and thus cause its apparent absorption; but if the humus contains little or no lime or magnesia this apparent absorption of phosphoric acid does not take place.

Humus substances probably possess some small absorptive power for whole salts.

Hydrated iron oxides and hydrated silicic acid rarely occur free in the soil to any great extent.

(4.) To the zeolite-like silicates is due the peculiar nature of clay soils. They have the property of drying to hard, compact masses, and also of remaining for a long time in suspension in pure water, but when in suspension, small quantities of acids, bases, and salts cause them to collect in flocks and to subside rapidly. The granular structure of a clay soil is chiefly due to the soluble salts, especially to calcium bicarbonate; the bases and salts absorbed by the colloids must also exert an influence. If the soluble salts are removed, the structure is altered and the clay becomes a mud.

These silicates are probably complex compounds of various colloidal silicates of aluminium, iron, the alkalis, and the alkaline earths, which contain also alkalis and alkaline earths in a state of absorption, but it is not possible to make out the exact relationship of the constituents. They can absorb free alkalis, alkaline earths, and ammonia from solutions, and they can also absorb bases by replacement from solutions of their salts. Potash is most strongly fixed by the soil,

and, consequently, is most strongly absorbed from saline solutions, replacing equivalent quantities of lime, soda, and magnesia. If a soil is treated with solutions of a potash, magnesia, soda or lime salt containing like amounts reckoning in equivalents, then the final strength of the potash-salt solution is less than that of the magnesia-salt solution, and that of the magnesia-salt solution is less than that of the soda- and lime-salt solutions, for the action of a dissolved lime, &c., salt on the absorbed potash is weaker than the action of a dissolved potash salt on the absorbed lime.

If a soil has been saturated with potash, &c., this can be replaced by repeated treatment with solution of another salt, for the potash, &c., extracted each time is removed and can exert no reversing action, and, further, each time the solution is weaker in potash and the reversing action is therefore less.

That soda salts promote an apparent absorption of phosphoric acid from a phosphate solution is explained by soda replacing lime and magnesia, which then produce a precipitate of calcium and magnesium phosphates.

Treatment of a soil with strong hydrochloric acid decomposes, to a great extent, those silicates to which the absorption, accompanied by exchange of bases, is due, although the soil still retains much aluminium silicate and aluminium potassium sodium silicate.

In addition to absorption by exchange of bases, the colloïd silicates can absorb the alkalis and alkaline earths as wholes, and they can also absorb salts as wholes, though their power to do the latter is feeble.

The conditions of absorption as it occurs in the soil in nature are not exactly the same as in experiments; for example, in nature the final equilibrium is rarely reached; and in experiments the soil is shaken with proportionally large volumes and proportionally concentrated solutions. The results of absorption experiments are only of limited value as a guide to the fertility of a soil, and must be considered in connection with the results of analysis; they cannot supersede the latter.

H. H. R.

Rapid Fermentation of Grape-juice. By A. AUDOYNAUD (*Ann. Agronom.*, 14, 211—221).—Many salts added to the juice in small proportion (0.5—1 gram per kilo. of fresh grapes) increase the vitality of the yeast. Most active are ammonium sulphate, phosphate, and carbonate, probably because they supply nitrogen to the yeast plant in a more available form than the albuminoids of the must. Nitrates cannot be substituted. Soluble calcium salts, such as the nitrate, sulphate, and bicalcic phosphate, also hasten the fermentation. Magnesium salts are far less efficacious. Boric acid is without action. The proportion of water has considerable influence on the rapidity of fermentation. The following conditions ensure great rapidity and regularity; water seven to eight times the weight of the sugar present; temperature 25°; ammonium carbonate and bicalcium phosphate each added in the proportion of 500 grams per 1000 kilos. of grapes; the must must remain acid after all these additions.

J. M. H. M.

Effect of Nitrogenous Manures on Tobacco. By C. O. HARZ (*Ann. Agronom.*, **14**, 234—235, from *Bot. Centralbl.*, **33**, 218).—From two years' experiments on small plots the author concludes that sun is more favourable than shade to the amount of crop and to its richness in nicotine, and that ammonium sulphate is better than an equivalent quantity of sodium nitrate. J. M. H. M.

Organic Nitrogenous Manures. By A. PETERMANN (*Bied. Centr.*, 1888, 366—367).—The percentage of nitrogen in waste wool, blood and leather meal, which were used in experiments on roots during 1885, 1886, and 1887, are here given, as also that contained in various cakes used as manures. The percentage of sugar in the roots as affected by the manures is also stated. E. W. P.

Analytical Chemistry.

Improved Wash-bottle. By J. SOBIECZKY and V. HÖBLING (*Zeit. anal. Chem.*, **27**, 365—366).—To prevent the retreat of the liquid from the point of the jet, and the consequent forcible ejection of the first drop when recommencing to blow into the bottle, a small Bunsen valve, made with very thin caoutchouc tube, is attached to the swan-neck tube in such a way as to lie within the rubber connection which gives flexibility to the jet. M. J. S.

Different Methods of Estimating Chlorides in Urine. By BRIGNONE (*Chem. Centr.*, 1888, 808, from *Ann. Chim. Farm.*, **7**, 137—159).—The different methods of estimating chlorine in urine, both directly and after destruction of the organic matter, are fully discussed. The author gives the preference to those processes in which the organic matter is previously destroyed by fusion with nitre. A process is also mentioned in which the organic matter is oxidised with potassium permanganate, and the titration of chlorine made directly with silver nitrate and potassium chromate; sulphates and nitrates act injuriously. Denigés' process, which seems to be the same as the above, gives higher results than any other method. The results are, however, sufficiently accurate for clinical purposes, and the process is simple to carry out. J. P. L.

Determination of Nitrogen by Soda-lime. By W. O. ATWATER (*Amer. Chem. J.*, **10**, 197—209).—It is unnecessary to powder the substance beyond allowing it to pass through a 1 mm. mesh. No loss of nitrogen by formation of alkaline cyanides need be feared if the soda-lime contain enough water and other conditions mentioned be adhered to, neither is there any loss of nitrogen gas except by oxidation of the ammonia. The most important error is caused by the formation of volatile nitrogenous compounds that pass through the

tube unchanged, and are not estimated either by standard acid or by platinum chloride; it is eliminated in most cases by packing the tube as described (this vol., p. 752), but in other cases where leucine-derivatives are dealt with or quinoline-derivatives are volatilised, these precautions are totally inadequate. The formation of red coloured substances or of a turbidity in the absorbing acid is no proof that the result is inaccurate.

H. B.

Estimation of Total Nitrogen in Organic Compounds. By P. CAZENEUVE and L. HUGOUNENQ (*J. Pharm.* [5], 17, 545—547, 593—594).—The authors modify Dupré's improvement of Dumas' method, and proceed as follows:—At the bottom of a combustion tube 15 cm. long is placed some dry manganese carbonate. This source of carbonic anhydride is preferred as it can be easily dried, its decomposition is indicated by change of colour, and on cooling it does not reabsorb carbonic anhydride. The remainder of the tube is charged as usual, and connected with a pump and manometer. To remove the air, the tube is exhausted three times successively, and each time carbonic anhydride is expelled from the manganese carbonate until the mercury descends completely; then, Dupré's apparatus is applied whilst the carbonic anhydride is still being evolved, and the combustion proceeded with in the ordinary way. Urine is very satisfactorily treated by mixing 5 c.c. with 5 grams of dry plaster of Paris as indicated by Washburne, together with 0.05 gram oxalic acid. After drying on the water-bath, the mass is intimately mixed with 30 grams of copper oxide and burned as above.

J. T.

Determination of Ammonia in Urine. By C. WURSTER (*Zeit. anal. Chem.*, 27, 406—407, from *Centr. Physiol.*, 1887, 485).—The mixture of the urine with baryta-water is placed in a flask, the bottom of which just touches a water-bath kept at 50°. At this temperature urea is not decomposed by baryta. The flask is connected with a second which plunges completely into the water of the bath and serves for arresting froth. This is followed by a bulb absorption apparatus, containing titrated acid, standing in cold water, and connected with the air-pump. About two-thirds of the mixture is distilled over whilst working the pump. Air is admitted to the overflow flask before disconnecting, and the residual acid is titrated.

M. J. S.

Estimation of Phosphoric Acid in Basic Slag. By J. H. VOGEL (*Chem. Zeit.*, 12, 85—86).—The author recommends the following modified form of Müller's method of estimating phosphoric acid in basic slag, as more convenient and quicker than the original. 5 grams of the slag is dissolved by heating for half an hour in a half-litre flask with 40 c.c. of water and 40 c.c. of hydrochloric acid, sp. gr. 1.12 (compare Kennepohl, this vol., p. 321), it is then filled to the mark and filtered. 50 c.c. of the solution is mixed with 10 c.c. of a 50 per cent. solution of citric acid, nearly neutralised with 10 per cent. ammonia, 20 c.c. of magnesia mixture gradually (during two minutes) dropped and stirred in, finally 10 to 12 c.c. of concentrated ammonia is added and the whole shaken round for a minute. As a

rule after two hours the solution may be filtered and proceeded with in the usual manner.

D. A. L.

Estimation of Manganese in Pig-iron, Steel, &c. By G. WEISSMANN (*Chem. Zeit.*, **12**, 205).—Manganese may be accurately determined in iron, &c., in the following manner:—0.4 gram of borings is dissolved in 30 to 40 c.c. of a solution, consisting of 10 parts of concentrated nitric acid, 10 parts of water, and 2 parts of concentrated sulphuric acid; 4 to 5 grams of chemically pure lead oxide is then added with vigorous shaking, the whole boiled for two or three minutes, and this operation again repeated. After settling, the permanganic acid is filtered through ignited asbestos and titrated with ammonium ferrous sulphate solution and dilute permanganate (1 gram in a litre). An estimation occupies at the most an hour, and concordant results have been obtained by this method with irons containing 2 to 3 per cent. of manganese. The operations should succeed one another without intermission, and should be conducted in a room not exposed to sunlight.

D. A. L.

Estimation of Lead in Tin Alloys. By Y. SCHWARTZ (*Chem. Zeit.*, **12**, 52).—One gram of the lead-tin alloy, rolled moderately thin, is warmed gently with 20 c.c. of hydrochloric acid until action ceases, which takes about half-an-hour; without removing any undissolved metal, bromine is added until solution is complete, and the liquid yellow in colour. The excess of bromine is boiled off, the solution diluted to 100 c.c., allowed to cool, and then poured in a thin stream, which is constantly moved about, into a solution of 40 grams of commercial sodium sulphide in 150 c.c. of water. When the lead sulphide has settled, it is separated, washed with dilute ammonium sulphide (containing 1 vol. ammonium sulphide prepared from commercial 10 per cent. ammonia to 9 vols. of water), converted into sulphate, and weighed as such. The lead sulphate is then dissolved in basic ammonium tartrate, and any insoluble tin oxide is collected and allowed for.

D. A. L.

Separation and Estimation of Antimony and Tin. By LOVITON (*J. Pharm.* [5], **17**, 361—363).—Antimony can be completely precipitated as sulphide in a solution containing equal volumes of water and hydrochloric acid of 22° B., whilst the precipitation of tin begins only in a solution containing at least three volumes of water to one of acid. This is used qualitatively by dissolving the alloy in concentrated hydrochloric acid with the addition of a few drops of nitric acid or a little potassium chlorate, then diluting the solution so that only the antimony is precipitated by hydrogen sulphide. The antimony sulphide rapidly settles, and the liquid is filtered through glass-wool, as paper will not withstand the strong acid, and the precipitate is washed with a liquid formed of one volume hydrochloric acid of 22° B., and one and a half volumes of hydrogen sulphide water. The filtrates are sufficiently diluted, and hydrogen sulphide is passed through to complete the precipitation of the tin. The separated metals can be estimated by dissolving in a freshly prepared solution

of sodium sulphide, and electrolysing in Riche's apparatus with a couple of Bunsen cells. This method of separation seems to be applicable to some other members of the group of metals precipitable by hydrogen sulphide. J. T.

Application of Diazo-compounds to the Detection of Organic Matter in Water. By P. GRIESS (*Ber.*, 21, 1830—1832).—Very small quantities of organic substances present in water can often be detected by means of diazo-compounds, of which diazobenzene sulphate is the most suitable. Two to four drops of a freshly prepared 1 per cent. solution of diazobenzene sulphate, made slightly alkaline with soda, are added to the sample of water placed in a colourless glass cylinder, and the mixture stirred. If no change of colour occurs within five minutes, the almost complete absence of human or animal excreta or putrefying matter may be inferred, but a yellow coloration shows the presence of larger or smaller quantities of such impurities. One part of human urine in 5000 parts of water and 1 part of horse's urine in 50,000 parts of water can be recognised with certainty. Good spring water gives no coloration, but when 100 c.c. of such water is mixed with several drops of waste water from a town canal, the reaction is, as a rule, at once perceptible. 100 c.c. of water, containing $\frac{1}{10}$ c.c. of normal human urine, gives, with this reagent, the same shade as is produced by Nessler's solution in an equal quantity of water containing $\frac{1}{20}$ mgm. of ammonia.

Substances containing sugar, even when present in relatively large quantities, cannot be detected by this method with any degree of certainty. Diabetic urine, containing 6 per cent. of grape-sugar, gave, after suitable dilution, a far less intense coloration than an equal quantity of normal human urine. F. S. K.

Incineration of Organic Substances. By H. KRONBERG (*Chem. Zeit.*, 11, 1600—1601).—For substances that swell up or explode, or fall to powder when heated, the author recommends burning a small portion of the substances in a covered platinum crucible over a bunsen, breaking up the burnt mass with a piece of platinum wire, and when moderately cool adding a further portion of the substance, repeating the operations until sufficient substance has been burnt. The incineration is complete in the manner recommended by Kobrich (this vol., p. 325). The platinum wire used as a stirrer is weighed with the crucible and contents, a slit is made in the side of the crucible lid for its support. D. A. L.

Detection of Impurities in Alcohols. By X. ROCQUES (*Compt. rend.*, 106, 1296—1298).—If pure benzene is used in Godefroy's process (this vol., p. 875), the results are not sensibly different from those obtained by Savalle's test with sulphuric acid alone. If, however, the so-called pure benzene of commerce is employed, a coloration is obtained even with pure alcohol, and in presence of aldehydes the coloration is much darker than with sulphuric acid alone. The author concludes that the addition of pure benzene does not increase the delicacy of the action of sulphuric acid, the results obtained by

Godefroy being due to the presence of impurities in the benzene used. In the absence of aldehydes, the addition of benzene does not increase the efficiency of sulphuric acid as a reagent for the detection of the higher alcohols. C. H. B.

Behaviour of Catechol with Fehling's Solution. By A. WOHL (*Chem. Centr.*, 1888, 278, from *Deut. Zuckerind.*, **13**, 37—38).—In presence of a large excess of sugar, catechol appears not to interfere with the accuracy of the Fehling's method, in fact, 0.2 per cent. may be present without its causing any serious error. A much larger quantity of catechol appears to decrease the quantity of cuprous oxide precipitated, and the author suggests that the catechol acts the part of an oxygen carrier from the air, it having the property of absorbing free oxygen in a marked degree. J. W. L.

Supposed Reaction of Phloroglucinol. By P. CAZENEUVE and L. HUGOUNENQ (*Bull. Soc. Chim.*, **49**, 339—341).—The test for phloroglucinol given in many works, which consists in adding a solution of potassium nitrite to a mixture of aniline or orthotoluidine nitrate and a very weak solution of phloroglucinol, is useless as a qualitative reaction for the latter. The same, or a very similar reaction, is given by phenol, resorcinol, orcinol, α -naphthol and β -naphthol, in 0.05 per cent. aqueous solution. F. S. K.

Determination of Sugar by Alcoholic Fermentation. By M. JODLBAUER (*Chem. Centr.*, 1888, 769, from *Zeit. Rüb.-Zuck. Ind.*, **25**, 308—346).—In the present paper the author considers the practicability of estimating sugar by alcoholic fermentation. He finds that under certain conditions the products are constant, and these conditions are—(1.) The use of well-developed yeast taken from an active fermentation, and consequently free from metamorphic changes in its protoplasm. (2.) Maintenance of a definite relation between the amount of yeast and the amount of sugar; the yeast should not exceed 50 per cent. of the amount of sugar. (3.) Exclusion of free oxygen. (4.) The use of a nutrient solution suitable to the full development of the yeast, so that the latter may during fermentation repair its waste. Unless the cell is well nourished, decomposition is slow and incomplete. The most favourable temperature is 34°; the most favourable concentration, 8 per cent.

Of the fermentation products, carbonic anhydride is the simplest to determine, and also affords the most trustworthy results. Cane-sugar and anhydrous maltose give 49.04 per cent.; dextrose, 46.54 per cent. of carbonic anhydride. The duration of the fermentation is of course dependent on the variety of sugar. Cane-sugar requires twice the time that maltose and dextrose do. J. P. L.

Estimation of Sugar in Beet. By A. PETERMANN and others (*Bied. Centr.*, 1888, 408—412).—Petermann, having carefully examined all the best methods in use, states that (1) the rotatory power of saccharose is the same whether the solvent be water or 60 per cent. alcohol; (2) 85 per cent. alcohol removes all sugar from a well-made mash of

roots; (3) a solution of sugar in 60 per cent. alcohol is not decomposed at the boiling point of the solution; (4) 25 to 50 grams of a well-made mash may be considered as a sufficient quantity in which to estimate the average percentage of sugar; (5) those methods which depend on the mixing of beet-juice with a like volume of absolute alcohol, give results identical with those obtained by the ordinary methods; and as cold alcohol does not precipitate the non-saccharine matters, this modification has no advantage over the old methods; (6) the percentage of sugar obtained by digesting or extracting the mash with alcohol is, on the average, 0.5 per cent. lower than that obtained by the old process of polarisation; the causes of this error are that the analysed juice is not the natural or normal juice, non-saccharine matters are present, and the correcting factor 0.95 is incorrect. Pellet, however, comes to a conclusion opposite to that of Petermann, for he recommends the digestion with water as the most correct, convenient, and cheapest, and he considers that even after the alcohol has been in contact with the mash for half an hour, there is no certainty that all the sugar has been extracted, in fact he finds that 0.4 to 0.7 per cent. less is extracted than when water is employed, and when digestion has been allowed for an hour, the amount extracted is the same as when digestion with water has proceeded for only half an hour. Pellet recommends the following procedure: 52.1 grams of the mash for the German polariser, and 32.4 for the French, is introduced into a flask marked at 200 and 210 c.c., the interval between being graduated to 0.5 c.c., then 175 c.c. of water and 5 c.c. of lead acetate are added, the flask filled up to 200 c.c. with water, and heated for half an hour at 85—90°, then cooled, filled up to 201.5 c.c., shaken, and filtered. E. W. P.

Reduction of a Solution of Methyl-violet by Invert Sugar.

By A. WOHL (*Chem. Centr.*, 1888, 739, from *Zeit. Rüb-Zuck. Ind.*, **25**, 347—352).—This test for minimal quantities of invert sugar employed by Ihl (this vol., p. 876) has been submitted to further experiment. It is found that the time required for decolorising the solution becomes longer as the solution becomes weaker, and that it is also dependent on the alkalinity of the solution. In order to obtain comparable results, and an approximation of the amount of invert sugar present, it is expedient to maintain the alkalinity constant, which is too tedious for practical purposes. Other reducing substances which occur in raw sugar, and which are not precipitated by lead acetate, do not decolorise the solution during the short time it is boiled. Ammonium salts hinder or delay the reaction. J. P. L.

Estimation of Small Quantities of Sugar in Urine.

By A. POLLATSCHKE (*Chem. Centr.*, 1886, 768—769, from *Deut. Med. Wochens.*, **14**, 354—355).—The reaction with Fehling's solution is much clearer and sharper if the urine is first shaken with good animal charcoal (prepared with hydrochloric acid) and filtered. The substances which hinder the reaction are thereby removed. As a control the delicate phenylhydrazine test should be used.

J. P. L.

Detection of "Saccharin." By C. SCHMITT (*Zeit. anal. Chem.*, **27**, 396—397, from *Rep. anal. Chem.*, **7**, 37).—For the detection of Fahlberg's "saccharin" by converting it into salicylic acid, it is necessary to ensure the absence of tannin, since that substance also yields traces of salicylic acid when fused with sodium hydroxide. The insolubility of tannin in a mixture of equal parts of ether and light petroleum furnishes a convenient method. If salicylic acid is present, its amount may be colorimetrically determined and allowed for. For detecting saccharin in wine, 100 c.c. is strongly acidified, shaken three times with a mixture of ether and light petroleum, the ethereal extract mixed with soda solution (not potash), evaporated in a silver basin, and the residue fused with more soda for half an hour at 250°. The melt is dissolved in water, acidified with sulphuric acid, and shaken with ether. The residue from the evaporation of the ether is tested with ferric chloride for salicylic acid. M. J. S.

Modification of the Methyl-violet Reaction for the Detection of Free Hydrochloric Acid in Gastric Juice. By G. KOST (*Chem. Centr.*, 1888, 731, from *Centr. Klin. Med.*, **9**, 243—244).—Penzoldt found that peptone and albumin do not hinder the methyl-violet reaction if they are first precipitated with a 10 per cent. solution of tannin. The author has been enabled to corroborate this result in a number of cases of cancer of the stomach. For the diagnosis of carcinoma of the stomach, however, the modified process does not appear to be so trustworthy as the original one. It is at present chiefly of theoretical interest, as it has from another source led to a confirmation of Cahn and von Mering's statements regarding the uncertainty of the methyl-violet test, and the frequent occurrence of free hydrochloric acid in carcinoma of the stomach. J. P. L.

Behaviour of some Acids towards Chromic Acid and Permanganate. By T. SALZER (*Ber.*, **21**, 1910—1911).—When a solution of citric acid is coloured pale-yellow by a drop of potassium chromate solution, the colour remains unchanged, even after addition of sulphuric acid, for some days. A solution of tartaric acid similarly treated becomes colourless. The presence or absence of $\frac{1}{2}$ per cent. of tartaric in citric acid can be detected by extending the experiments over some hours.

Formic, acetic, succinic, and benzoic acids behave like citric acid, whilst lactic acid decolorises the chromate. Tannin and pyrogalllic acid produce dark colorations, and phenol and salicylic acid give orange-red colorations.

A solution of 0.1 gram of citric acid and 0.5 gram of sodium carbonate in 20 c.c. of water when treated with a drop of a solution of potassium permanganate (1:500) remains coloured; if 0.1 gram of tartaric acid is treated in a similar manner, the solution becomes colourless in 5 to 10 minutes (compare v. Baeyer, *Annalen*, **245**, 103).

N. H. M.

General and Physical Chemistry.

Refractive Indices of the Metals. By A. KUNDT (*Ann. Phys. Chem.* [2], **34**, 469—489).—Determinations of the refractive indices of various metals, and more especially silver, have been made by several observers, but the results obtained are not by any means concordant. Quincke made use of various interference methods, and Wernicke of an absorptive method; Quincke's different determinations gave very different results, and whilst Wernicke gives a value between 3 and 5 for the refractive index of silver, Voigt concludes from the same experiments of Wernicke's, that its value is about 0.25 (Voigt, *Ann. Phys. Chem.* [2], **23**, 104 and 2595). Beer (*Ann. Phys. Chem.*, **92**, 402) and Voigt, by the aid of both Cauchy's and Voigt's theories, have also calculated the velocity of light in various metals from reflection experiments, and in each case they came to the conclusion that Snellius's law of refraction did not hold; the author, however, retains the definition of the index of refraction as the ratio of the velocity of light in a vacuum to that in the metal. The results obtained by Beer and by Voigt agree fairly well, and they both find that the index of refraction is less than unity for silver and gold, approximately equal to unity in the case of copper, and greater for other metals.

All these observers made use of indirect methods, but the author having overcome the difficulty of obtaining prisms of the various metals sufficiently thin to be transparent, measures the index directly from the refraction of the light traversing these prisms.

The basis of each prism consisted of a thin platinised glass plate, the platinum deposit being so uniform that no variation could be detected even under a high magnifying power. The metallic prisms were formed on this in most cases by electrolytic deposition, the method adopted being to place a thin sheet of the required metal perpendicular to but not quite touching the platinised glass, and to use this plate as the anode, the electrolytic liquid being retained as a capillary film between the edge of the metal plate and the glass. In the case of silver, a chemical reduction method due to Quincke was also employed, and as it was found impossible to obtain platinum prisms by electrolysis, they were formed by placing a strip of platinum foil perpendicular to the glass plate, and deflagrating it by a strong current, when it was deposited in a double wedge upon the glass. The prisms were carefully tested to ensure the surfaces being truly plane, by examining the reflection of a pair of fine crossed fibres, and the defective ones, which amounted to a large proportion of the whole, were rejected.

The following table gives the mean values obtained for the relative coefficients of refraction with respect to air, for red, white, and blue

light respectively. In the case of silver, the dispersion was too small to be determined.

Metal.	Mean values of μ .		
	Red.	White.	Blue.
Silver	—	0·27	—
Gold	0·38	0·58	1·00
Copper	0·45	0·65	0·95
Platinum	1·76	1·64	1·44
Iron.....	1·81	1·73	1·52
Nickel.....	2·17	2·01	1·85
Bismuth	2·61	2·26	2·13

The table shows that except in the cases of silver, which gives no appreciable dispersion, and of gold and copper, in which the dispersion is normal, all the metals examined produce anomalous dispersion.

Some experiments were made with prisms formed of iodide of silver formed by iodising a silver prism, and oxides of iron, nickel, bismuth, and copper, formed by heating prisms of the pure metal in the air. The results obtained are given below.

	Values of μ .		
	Red.	White.	Blue.
Iodide of silver	—	2·31	—
Oxide of iron.....	1·78	2·11	2·36
Oxide of nickel	2·18	2·23	2·39
Oxide of bismuth	—	1·91	—
Oxide of copper.....	2·63	2·84	3·18

Prisms formed of mixtures of platinum and gold with their oxides were also experimented on, but the values obtained varied considerably, owing doubtless to variations in the proportion of oxide present.

The results of the experiments appear to indicate that the velocities of light in different metals are in much the same proportion as the conductivities for electricity and heat. Thus taking the velocity in silver as 100, the velocities in the other metals are as below :—

Silver.	Gold.	Copper.	Platinum.	Iron.	Nickel.	Bismuth.
100	71	60	15·3	14·9	12·4	10·3

which correspond very closely with the relative electrical conductivities, except in the cases of copper and bismuth. The small value obtained for copper is probably due, as the author suggests, to

the unavoidable presence of oxide, which increases the value of μ , and, as is well known, the slightest traces of oxide largely diminish the electrical conductivity. In the case of bismuth, the authors point out that all the determinations of electrical conductivity have been made with crystalline specimens, for which the conductivity would probably be lower, whilst in the bismuth prisms used in these experiments no traces of crystalline structure was observable.

The author suggests that it would be of interest to further test the reality of the correspondence indicated, by endeavouring to determine whether μ increases with the temperature, in which case the velocity of light in the metal, like the electrical conductivity, would diminish with increase of temperature, and also whether magnetisation produces any effect on the value of μ , analogous to the different electrical conductivity in different directions, which is known to be produced in this manner.

G. W. T.

Molecular Refraction of some Bromine-derivatives of Ethane and Ethylene, and the present Position of the Landolt-Brühl Theory. By R. WEEGMANN (*Zeit. physikal. Chem.*, 2, 218—240, and 257—269).—These researches were undertaken with the object of testing the theories put forward by Landolt and Brühl of the connection between molecular refraction and chemical constitution, by the examination of a series of substances of simple, well-known constitution, but with high specific gravity and large refractive power, such as the bromine-derivatives of ethylene and ethane. The following table contains a list of the substances examined, together with the observed density d at 20° compared with that of water at 4° , and the refractive index n for the D line of the spectrum, and a temperature of 20° .

		$d.$	$n.$	$\frac{B}{d}$
Ethylene chloride	$C_2H_4Cl_2$	1·25014	1·144387	0·35625
Ethylidene chloride.....	$C_2H_4Cl_2$	1·17503	1·416785	0·35623
Ethylene bromide	$C_2H_4Br_2$	2·17681	1·537888	0·34311
Ethylidene bromide	$C_2H_4Br_2$	2·05515	1·512767	0·34314
Acetylene tetrabromide ...	$C_2H_2Br_4$	2·96725	1·637951	0·33739
Acetylidene tetrabromide .	$C_2H_2Br_4$	2·87482	1·627721	0·35515
Acetylene dibromide.....	$C_2H_2Br_2$	2·22889	1·543368	0·39949
Tribromethylene	C_2HBr_3	2·68762	1·599195	0·38881
Vinyl tribromide.	$C_2H_3Br_3$	2·57896	1·589922	0·33868
Ethyl bromide.....	C_2H_5Br	1·45551	1·423865	0·34138
Aniline	C_6H_7N	1·02904	1·586321	1·34812
Benzene	C_6H_6	0·87907	1·501442	1·02886

The refractive index of each substance was also measured for the lines K, α , β , and γ , and for temperatures from below 10° to above 30° . The last column of the table contains the value of the second constant B in Cauchy's dispersion formula calculated from n_α and n_γ ,

$$3 \times 2$$

and may be taken as a measure of the dispersive power, divided, in order to free it from the influence of the density, by d . This gives to some extent a measure of the influence of constitution on the dispersion, and it is of interest that those substances containing a double bond give a nearly constant value of about 0.4, while the rest vary from 0.34 to 0.36. In other respects, Cauchy's formula was wholly unsatisfactory as an interpolation for refraction of different wave-lengths. The dispersion formula of Ketteler gave somewhat better results.

The specific refraction as given by both the formulæ $(n - 1)/d$ and $(n^2 - 1)/(n^2 + 2)d$ was calculated for each substance for the temperatures 10°, 20°, and 30°, and from this the molecular refraction. The specific refraction is not absolutely constant for the same substance, for the values given by the n formula decrease slightly with temperature, whilst those of the n^2 formula increase. This increase or decrease affects only the fourth decimal place for the 20° interval examined with either of the above formulæ; to three places of decimals, therefore, the constancy holds for this interval. The molecular refraction gives values on the whole confirmatory of the Landolt-Brühl theory. Differences which appear between the calculated values and those observed, may to some extent be explained by the want of constancy in the specific refraction, although probably chiefly due to the influence of dispersion. It is also found that of two isomeric substances the normal one always gives the smaller value for the specific refraction calculated by the n^2 formula. The two groups, acetylene dibromide, $C_2H_2Br_2$, ethylene or ethylidene bromide, $C_2H_4Br_2$, and tribromethylene, C_2HBr_3 , vinyl tribromide, $C_2H_3Br_3$, form exceptions to the rule that substances containing a double bond have a specific refraction greater than, or at least equal to, that of compounds containing two additional hydrogen-atoms without the double bond. The atomic refraction of bromine calculated from the n_a values is for the n formula 15.38, and for the n^2 formula 8.83, as means of the experiments. H. C.

Luminescence of Pyrogallol. By P. LENARD and M. WOLF (*Ann. Phys. Chem.* [2], **34**, 918—925).—The authors, without knowing of the similar observations previously made by Eder (*Photogr. Mitt.*, No. 344), observed that when a photographic plate after development with an Eder potash developing solution, or with a soda developer after previous washing with a solution of alum, becomes distinctly luminous and remains so for a couple of minutes or so. The phenomenon appeared to them to be of sufficient interest to call for further investigation, and a number of experiments made with a view of determining the origin of the luminosity are described in the paper.

As the phenomenon was found not to be a case of true phosphorescence, they call it "*luminescence*."

From their investigation, they arrived at the conclusion that the phenomenon is due to both pyrogallol and oxygen being condensed on the surface of the freshly precipitated alumina, resulting in rapid oxidation.

In general the luminosity was not observed when sodium sulphide was not present, but they found that a feeble luminescence could even then be produced by saturating potassium pyrogallate with pure oxygen and then adding a solution of alum. From this and other experiments they conclude, that the part played by the sodium sulphide is to delay the oxidation until the pyrogallol and oxygen have been brought into close contact in the pores of the precipitated alumina.

G. W. T.

Fluorescence of Ferruginous Calcium Oxide. By L. DE BOISBAUDRAN (*Compt. rend.*, 106, 1708—1710).—If calcium carbonate is mixed with a small quantity of ferric nitrate and strongly heated, the calcium oxide obtained shows a green fluorescence, which is sometimes very intense, but gives no definite spectrum. With only a few tenths of a per cent. of ferric oxide, the green fluorescence is well developed, and is less blue than that obtained in presence of copper. As the proportion of ferric oxide is reduced, the fluorescence gradually changes to that of pure calcium oxide. Similar results were obtained with ferric nitrate which had been purified by means of hydrogen sulphide. There can be no doubt that this green fluorescence is really due to iron and not to copper.

C. H. B.

Degree of Oxidation of Chromium and Manganese in Fluorescent Mixtures. By L. DE BOISBAUDRAN (*Compt. rend.*, 106, 1781—1784).—The green fluorescence shown by calcium oxide containing chromium is replaced by a white fluorescence if the mixture is strongly heated in a current of hydrogen. It is not due either to copper or to iron, and the fluorescence of calcium oxide containing lead is pale-yellow. All the specimens of calcium oxide which show this green fluorescence contain more or less chromium in the form of chromate.

C. H. B.

Photochromatic Properties of Silver Chloride. By G. STAATS (*Ber.*, 21, 2199—2200).—The author endeavoured to isolate the coloured substances formed on silver plates when the latter are treated with ferric chloride covered with variously coloured glasses, and exposed to sunlight (compare Abstr., 1887, 1671). Carey Lea's method (this vol., p. 1) was employed, but photo-red was obtained in all cases. Photo-red is produced when a silver plate of any colour is warmed. As soon as the superficial layer of the colour is treated with solvents, the colour is destroyed, but when very thin plates of chemically pure silver are treated with a solution of ferric chloride on one side only, then exposed in the usual manner until the red and violet colours appear, and finally dissolved in nitric acid, both the red and violet separate unchanged in thin plates, which are generally bounded by straight lines.

The separated silver chloride which has not been coloured is built up of small yellow plates.

F. S. K.

Constant Battery with a Negative Electrode of Carbon. By FABINGI and FARKAS (*Compt. rend.*, 106, 1597—1598).—In this

battery the negative electrode consists of carbon and the positive electrode of platinum, and there are two electrolytes, namely, fused sodium or potassium hydroxide, and the product of the action of fused sodium hydroxide on platinum, $\text{Na}_2\text{O.PtO}_2 + 6\text{H}_2\text{O}$, or $2\text{Pt(OH).ONa} + 3\text{H}_2\text{O}$. The latter compound covers the internal surface of a small platinum capsule, which is then filled with sodium hydroxide, previously fused in a silver dish. A small gas flame serves as a source of heat, and an electrode of gas carbon is immersed in the fused sodium hydroxide, the whole apparatus being protected from draughts, &c., by a screen. When the circuit is completed the electromotive force quickly reaches a certain value, and the action then becomes stationary. The electromotive force varies in the same direction as the temperature in the neighbourhood of the carbon, and in the opposite direction in the neighbourhood of the platinum, and, other conditions being equal, the intensity of the latter is greater than that of the former. When the two temperatures are equal, the electromotive force varies in the same direction as the temperature. When the variations in the height of the flame are small, and the loss of fused sodium hydroxide does not exceed a certain limit, the variations in the electromotive force are inappreciable. Sudden and considerable variations in the external resistance of the circuit produce only very brief temporary variations in the difference of potential between the two electrodes.

C. H. B.

Use of Magnesium in Primary Batteries. By C. HEIM (*Electrotechnische Zeitschrift*, **8**, 472—476, and 517—524).—These investigations were undertaken with a view to utilise magnesium practically for primary batteries for laboratory use, as recently invented methods of manufacture enable it to be produced at a much lower cost than formerly.

The temperature of observation was in every case between 17° and 21° . The following solutions were used throughout the experiments; the specific gravities being determined at a temperature of 15° . Dilute sulphuric acid, 1.026; magnesium sulphate, 1.223; magnesium chloride, 1.170; sodium chloride, 1.155; copper sulphate, 1.187.

The values of the E.M.F. given by a zinc-magnesium couple in a single fluid were in volts:—

In sulphuric acid, 0.876; in magnesium sulphate, 0.784; in magnesium chloride, 0.769; in sodium chloride, 0.616.

The values of the E.M.F. obtained by replacing the zinc in a Daniell, Bunsen, dichromate, and Leclanché cell respectively are given opposite, the E.M.F. of the normal cell being given for comparison.

The dichromate solution consisted of 92 parts potassium dichromate, 172 parts sulphuric acid, and 900 parts water, as used by Bunsen. At 15° its specific gravity was 1.140. The specific gravity of the concentrated solution at the same temperature was 1.261.

Of the different cells experimented with, the only ones found to be of practical value were the modifications of the Bunsen and Leclanché cells, in which magnesium in a solution of its sulphate or chloride was

Name of cell.	Anode.	Liquid or mixture surrounding anode.	Kathode.	Liquid surrounding kathode.	E.M.F. in volts.
Daniell	Copper ..	Copper sulphate	Zinc	Dilute sulphuric acid	1·183
	"	"	Magnesium.	"	2·033
	"	"	"	Magnesium sulphate	1·930
Bunsen	Arc lamp carbon	Nitric acid containing 68 p. c. of acid	Zinc	Dilute sulphuric acid	1·991
	"	"	Magnesium.	"	2·888
	"	"	"	Magnesium sulphate	2·863
	"	"	"	Magnesium chloride	2·910
	"	"	"	Sodium chloride	2·709
Dichromate .	Arc lamp carbon	Dichromate solution	Zinc	Dichromate solution	2·000
	"	"	Magnesium.	"	2·952
	"	"	Zinc	Dilute sulphuric acid	2·110
	"	"	Magnesium.	"	2·980
	"	"	"	Magnesium sulphate	2·900
	"	"	"	Magnesium chloride	2·970
	"	Concentrated dichromate solution	"	Dilute sulphuric acid	3·042
	"	"	"	Magnesium sulphate	2·971
	"	"	"	Magnesium chloride	3·046
Leclanché ..	Carbon ..	Mixture of coke and manganese dioxide in small grains	Zinc	Ammonium chloride	1·587
	"	"	Magnesium.	"	2·219
	"	"	"	Magnesium sulphate	2·334
	"	"	"	Magnesium chloride	2·364
	"	"	"	Sodium chloride	2·151

substituted for zinc in dilute sulphuric acid. Of these two solutions, the chloride is preferable, chiefly on account of its specific conductivity being about three times that of the sulphate. In the Bunsen cell, the initial E.M.F. is slightly higher with the chloride than with the sulphate, but it does not remain quite so constant. In the Leclanché cell, the initial E.M.F. is again slightly higher with the chloride,

but it also remains much more constant than when the sulphate is used.

The tables given below show the relative behaviour of these and the normal cells of equal dimensions. T is the time in hours from the closing of the circuit, E the E.M.F. in volts, R the internal resistance in ohms, and C the current in amperes through an external resistance adjusted to give as nearly as possible an initial current of 1 ampère.

Normal and Modified Bunsen Cells.

T.	Zinc in dilute sulphuric acid.			Magnesium in magnesium sulphate.			Magnesium in magnesium chloride.		
	E.	R.	C.	E.	R.	C.	E.	R.	C.
0	1.931	0.35	1.081	2.809	0.55	1.015	2.826	0.41	1.028
0.5	1.853	0.18	1.162	2.725	0.46	1.035	2.705	0.28	1.040
1	1.841	0.16	1.131	2.701	0.45	1.030	2.647	0.23	1.030
2	1.837	0.15	1.117	2.661	0.54	0.982	2.589	0.21	1.014
3	1.827	0.15	1.147	2.600	0.54	0.960	2.587	0.26	0.989
4	1.828	0.16	1.130	2.565	0.53	0.961	2.570	0.29	0.976
6	1.817	0.18	1.113	2.532	0.50	0.952	2.522	0.35	0.934
7	1.808	0.19	1.095	2.519	0.52	0.944	2.497	0.37	0.922
8	1.803	0.21	1.092	2.492	0.49	0.940	2.487	0.42	0.894
9	1.798	0.23	1.050	2.488	0.50	0.934	2.470	0.44	0.891

Normal and Modified Leclanché Cells.

T.	Zinc in ammonium chloride.			Magnesium in magnesium sulphate.			Magnesium in magnesium chloride.		
	E.	R.	C.	E.	R.	C.	E.	R.	C.
0	1.646	2.4	0.1019	2.300	3.8	0.1013	2.306	2.5	0.1009
0.5	1.451	1.1	0.0977	2.199	3.2	0.0991	2.222	2.2	0.0988
1	1.428	1.1	0.0960	2.152	3.1	0.0976	2.180	2.2	0.0970
2	1.396	1.1	0.0940	2.150	3.5	0.0954	2.157	2.2	0.0960
3	1.368	0.95	0.0930	2.072	3.1	0.0939	2.132	2.2	0.0951
4	1.355	0.91	0.0924	2.047	3.1	0.0925	2.120	2.2	0.0945
6	1.333	0.85	0.0910	2.014	3.2	0.0906	2.098	2.3	0.0933
7	1.323	0.84	0.0907	2.006	3.4	0.0897	2.090	2.2	0.0930
8	1.306	0.72	0.0900	1.994	3.4	0.0891	2.090	2.2	0.0927
9	1.309	0.81	0.0895	1.983	3.4	0.0886	2.074	2.2	0.0927

These modifications of the Bunsen cell are suitable for use where a strong current is often required for a moderate time, and the modifications of the Leclanché where a high and constant E.M.F. is required to give a small current through a large resistance.

G. W. T.

Determination of the Potential Differences between Mercury and Electrolytes. By R. BLONDLOT and E. BICHAT (*Zeit. physikal. Chem.*, **2**, 98—99).—Reply to objections raised by Ostwald against the accuracy of the authors' method of experimenting, in which, while admitting that the method devised by the latter is easier of performance and leads to better results, their own is defended in point of accuracy.
H. C.

Electrolysis with Alternating Currents. By G. MANEUVRIER and J. CHAPPUIS (*Compt. rend.*, **106**, 1719—1722; and **107**, 37—40).—When an alternating current is passed through an ordinary voltmeter containing acidulated water, there is usually no appreciable decomposition. If, however, electrodes of very slender platinum wire are used in place of platinum plates, there is an immediate and abundant evolution of gas. For a given intensity of current there is a particular area of surface of electrode from which no gas is evolved, or in other words, with which no electrolysis takes place, but if the surface is gradually reduced by reducing either the length or breadth of the electrode, evolution of gas begins, and is greater the greater the reduction of surface. Conversely, for an electrode with a given surface there is a particular intensity of current below which there is no evolution of gas. Above this limit electrolysis takes place, and increases with the intensity of the current. The gas evolved has the same composition in all cases, but the proportion of oxygen is less than one-third of the total volume. Ozone is produced in considerable quantity at both electrodes, notwithstanding the presence of hydrogen. The proportion varies with the intensity of the current, and also with the form of the electrodes.

The simultaneous presence of ozone and hydrogen at the electrodes points to their reversion into water, and with platinum electrodes a determining cause is to be found in the condensing power of the surface of the metal, the condensing action being proportional to the area of surface.

With copper electrodes there is no evolution of gas, even when the intensity of current is sufficient to produce electrolysis with platinum electrodes, but the surface of the copper becomes covered with reduced copper, and hence it is evident that the ozone converts the copper into oxide, and the latter is reduced by the hydrogen. If copper wire is employed for the electrodes there is evolution of gas, but the action soon ceases, since the wire disintegrates and falls to the bottom of the voltmeter in the form of reduced copper.

Mercury electrodes with a large surface cause a slight evolution of hydrogen, and the surface of the metal becomes covered with mercurous sulphate. Under similar conditions a continuous current gives mercuric sulphate.

It is evident from these observations that the primary and secondary reactions with alternating currents are very different from those obtained with direct currents.

When an alternating current of 2.5 ampères is passed through a voltmeter with platinum electrodes containing a solution of copper sulphate, there is considerable development of heat, but no electro-

lysis. If, however, the electrodes are reduced to 0.1 mm. diameter and 20 mm. in length, gas is evolved, and copper is deposited. The same phenomena are observed with electrodes of copper, but the latter are gradually converted into spongy reduced copper, the metal being alternately oxidised and reduced.

In electrolysis with alternating currents, a condition of equilibrium is always possible between the velocity of electrolytic decomposition and the velocity of recombination of the constituents of the electrolytes. The chief cause tending to increase the rate of decomposition is the intensity of the current. The electrodes may also exert considerable influence either by taking part in the chemical change or by reason of their physical properties. Other conditions being equal, the frequency of alternation of the current is an important factor. If the alternations are comparatively slow, there is sufficient time for the products of decomposition to diffuse away from the immediate neighbourhood of the electrodes, and therefore out of the sphere of possible recombination.

By means of a dynamo with separate excitation, the authors were able to vary the rate of alternation of a current whilst keeping its intensity constant. In one experiment the intensity of the current was adjusted so that with 2000 alternations per minute there was no electrolysis of acidified water, but if this was reduced to 1500, there was an abundant evolution of gas. In another case there was a regular evolution of gas with 2000 alternations per minute, but when this was increased to 2600, decomposition ceased. Similar effects are produced by varying the superficial area of the electrodes.

C. H. B.

Alternate Current Electrolysis. By W. E. AYRTON and J. PERRY (*Electrician*, 21, 299—300).—This paper contains an account of some detailed experiments made under the authors' direction by Messrs. Raine, Lamb, Smith, and Priest, and was published in its present fragmentary form in connection with the paper recently communicated to the French Academy by Maneuvrier and Chappuis (preceding Abstract).

The authors state that with an ordinary voltameter no evolution of gas is as a general rule observed with alternate currents. In the Central Institution experiments, on the contrary, alternate currents passed through an ordinary Hoffmann voltameter containing a 33 per cent. solution of sulphuric acid, always caused an evolution of gas. The gas comes off, as far as can be seen, from the wires instead of from the plates, as with direct currents, and the liquid is found to get rapidly hot, showing that there must be a good deal of decomposition and recombination of the gases. An alternate current of 3 ampères passing through a Varley resistance, made of flexible carbon cloth, in circuit with the voltameter, was found to heat the former much more than a direct current of the same strength. This was probably due to the rapid decomposition and recombination of the moisture on the cloth.

According to Maneuvrier and Chappuis, a current density of at least 3 ampères per sq. cm. is requisite to produce visible decomposition, whilst according to these experiments a current-density of less

than one-third of this, counting only one surface of each plate, or one-sixth, counting both surfaces, is required, unless practically the whole of the current is to be supposed to pass from wire to wire, and none to leave the plates.

The rate of alternation in the experiments was about 10,080 per minute.

When the speed of the dynamo was increased, thereby increasing the rate of alternation, the decomposition became much less, although the current at the same time increased from 3 to $4\frac{1}{2}$ ampères. The speed was then lowered until the current was again 3 ampères, but the decomposition was still much less than in the first case, while gas was evolved about twice as fast at one electrode as at the other, the former consisting of nearly pure hydrogen, and the latter of an explosive mixture. When the same voltameter was used again, gas came off freely from one electrode and not from the other, and when the dynamo terminals were reversed, the gas continued to come off only from the same electrode as before. When a direct current was used, gas came off freely from both electrodes, but on passing an alternate current again, the same thing occurred just as before.

In some further experiments with about 10,000 alternations per minute, it was found that one electrode, say P, was better able to produce visible decomposition than the other, Q. The superiority of P over Q was gradually diminished by sending a direct polarising current from Q to P through the voltameter, and finally the superiority was reversed. When the direct polarisation current was reversed P gradually regained its superiority. With an alternate current of $2\frac{1}{2}$ ampères, and a direct polarising current of 6 ampères, it was found possible to cause the former to produce rapid decomposition at either of the electrodes at will, and no visible decomposition at the other electrode, by previously sending for some time the 6 ampère current through the liquid from that electrode at which subsequent decomposition by the alternate current was desired.

It seems, therefore, that a deposition of hydrogen on a platinum electrode hinders, and may even stop altogether all visible decomposition by an alternate current, while a deposition of oxygen on the other electrode does not hinder, but may even favour visible decomposition.

Further it appears that although the direct polarising current may be strong enough to produce rapid decomposition, the gases so produced do not affect in any marked way the subsequent relative decomposition produced at the two electrodes by an alternate current, when the alternate current exceeds some particular strength relatively to that of the previous direct polarising current.

G. W. T.

Electrolysis of Solutions of Potassium Hydroxide. By G. BERSON and A. DESTREM (*Compt. rend.*, 106, 1794—1797).—When a solution of potassium hydroxide is electrolysed with platinum electrodes, the volume of the oxygen evolved is always less than half that of the hydrogen, and the liquid near the positive electrode gives the reactions for hydrogen peroxide. With a positive electrode of

copper, a 50 per cent. solution of potash, and a current of 0.06 ampère, the extremity of the copper electrode blackens as soon as the circuit is closed, and a blue cupropotassium solution falls from it to the bottom of the voltameter. This black coating gradually spreads over the surface of the electrode, and as soon as it is completely covered, there is an evolution of gas, and the resistance of the electrolyte increases by about 50 per cent. The black layer of oxide gradually dissolves, forming a cupropotassium solution, and the perfectly clean copper electrode then behaves exactly like platinum. If the circuit is broken, and then quickly closed again, the electrode continues to behave like platinum, but if there is a considerable interval of time before the circuit is again completed, the black layer is again formed on the copper, and the series of phenomena is repeated. It would seem, therefore, that the insolubility of the copper is due to the formation of a layer of gas on the surface of the electrode.

For the same current and the same liquid, the time which elapses before the electrode is covered with oxide, and the evolution of oxygen begins, is proportional to the surface of the electrode, a fact which is readily illustrated by inclosing in the same circuit two voltameters, in one of which the positive electrode is a copper plate, and in the other a copper wire. For a given solution and a given electrode, the time is shorter the greater the intensity of the current. With weak currents, the layer of oxide does not dissolve. The time is also shorter the weaker the potash solution.

C. H. B.

Determination of the Size of the Molecules of Salts from the Conductivity of their Aqueous Solutions. By P. WALDEN (*Zeit. physikal. Chem.*, **2**, 49—77).—In continuation of the author's researches on the above (this vol., p. 891), it appears from the examination of the sodium salts of arsenious acid, that a tribasic acid does not exist, salts of the form $\text{As}(\text{OMe})_3$ being basic salts, and that arsenious acid in solution behaves as a dimeta-acid, having the molecular formula $(\text{AsO}\cdot\text{OH})_2$. It is shown that mono- and bi-sodium arsenates, both of which exist as such in solution, are converted respectively by heating wholly into the meta- and pyro-arsenates. Trisodium arsenate is unstable in solution, and decomposes with rising dilution. In arsenic acid, as in phosphoric acid, the three hydrogen atoms are of unequal value. The monosodium salt is strongly acid, the bisodium, which appears to be the normal salt, is neutral, and the trisodium is basic.

Hydrofluoric acid does not exist as bibasic acid, H_2F_2 , in dilute solution, but as the simple molecule HF , and the acid fluorides are decomposed into normal salt and free acid. Chloric, bromic, and also iodic acid are monobasic, the so-called acid iodates not existing in solution. Measurements with periodates show that of these only the mono-salt is stable, both sodium periodate and perchlorate being salts of monobasic acids. Increasing the amount of alkali results in the formation of unstable and basic salts.

The salts of the bibasic chromic acid are less stable than the isomorphous sulphates, but are better conductors. Acid salts of the form $\text{R}'\text{HCrO}_4$ do not exist. Di- and tri-chromates are unstable, and

do not exist undecomposed in solution. Platinocyanic and platinochloric acids are bibasic, the salts being atomic and not molecular compounds. Salts of the form $R'HPtCy_4$ do not exist in solution, but separate into neutral salt and free acid. Chromicyanic is analogous to ferricyanic acid and tribasic.

H. C.

Chromic Acid. By W. OSTWALD (*Zeit. physikal. Chem.*, 2, 78—80).—The results of Walden's researches on chromic acid (preceding Abstract) show that it cannot be included in the list of ordinary mono- or bi-basic acids, and this together with the high conductivity of its solutions, which appears from the very slight increase with rising dilution to be near its maximum, and general considerations of its behaviour, lead the author to conclude that in aqueous solution the acid exists not as H_2CrO_4 but as $H_2Cr_2O_7$. The following is brought forward in support of this.

From the recent investigations of the molecular reduction of the freezing point of water by various substances, it appears that the freezing point of a solution which contains in a kilogram 1 gram-molecule of any compound should be -1.85° ; or, in the case of an acid, if complete dissociation of the compound into its ions takes place, it is double this if the acid is monobasic and treble if it is bibasic. If instead of this equivalent normal solutions be taken, in the latter case the number for the bibasic acid would have to be halved, and thus give a value three-quarters of that for the monobasic acid. The following freezing points were observed for equivalent normal solutions: $C_2H_4O_2$ -1.92° ; HNO_3 -3.70° ; H_2SO_4 -2.00° ; H_2CrO_4 -1.34° . Acetic acid not being dissociated gives the normal value; nitric acid in which dissociation is nearly complete about double this; and sulphuric acid which is dissociated about 0.6; and the solution of which contains therefore $\frac{1}{2}(0.4 + 3 \times 0.6) = 1.10$ mol., should and does freeze at -2.00° . Chromic acid, if H_2CrO_4 , and in accordance with the conductivity dissociated one-half, should have the freezing point of a normal solution -1.85° , but if $H_2Cr_2O_7$, it follows from the conductivity that this would be completely dissociated, and that the freezing point of the solution should be $-1.85 \times \frac{1}{4} \times 3 = -1.39^\circ$. The number actually obtained is 1.34° .

H. C.

Apparent Manifestation of Chemical as Mechanical Attraction. By J. W. LANGLEY (*Zeit. physikal. Chem.*, 2, 83—91).—An arrangement was devised by which any change of weight in one of the electrodes of an electrolytic cell could be ascertained, and the current changed in direction at the will of the observer, so that this electrode might be converted into either positive or negative pole. In the first series of experiments, the electrodes were of copper. On immersing them in saturated copper sulphate containing only traces of free sulphuric acid and passing the current, in contradiction to the course of the experiment which requires the transference of copper from the positive to the negative pole, the positive pole was observed to gain in weight and the negative pole to become lighter, this change lasting for from 20 seconds to one minute, and then a gradual reversal set in and the normal action took place. From this it appears that

this change may be divided into two epochs, the first a variable and reversible one, and the second permanent.

A similar peculiarity was noted for solutions of the following salts, the electrodes being in each case the same metal as that of the salt: $\text{Cu}(\text{NO}_3)_2$, ZnSO_4 , ZnCl_2 , ZnBr_2 , ZnI_2 . The acetates of copper, zinc, and lead act normally, and from this and slight differences observed with salts of the same metal, it appears that the change depends primarily on the character of the negative radicle. The acetates probably only form an apparent exception, their behaviour being due to the comparatively feeble acidity of acetic acid, as no change in weight whatever occurs in either electrode until after the first 10 or 20 seconds of the current, the permanent change then gradually setting in. Experiments were then made with free acids which show more clearly that the variable epoch depends in the first degree on the nature of the negative radicle. The metals zinc, copper, mercury, and platinum all give the variable increment in weight at the positive pole, the strength of the acid solution making little or no difference.

On weighing the electrodes before and after electrolysis, it was found that both during the variable and permanent epoch the positive pole was losing in weight. The phenomenon of the variable epoch must therefore be caused by some change in the solution surrounding the electrode and not in the electrode itself. By further experiments it is shown that a concentration of the negative radicle takes place round the positive pole. This concentration, due to the affinity of the metal of the electrode for the negative radicle, is, according to hypothesis, the result of a linear attraction extending to a distance far exceeding the radius of one molecule and of an elective kind. While this attraction is in force, that is, during the passage of the current, a layer of molecules of the negative radicle is produced on the positive electrode, thus causing its increase in weight.

H. C.

Expansion, Compressibility, and Specific Heat of Solutions of the Chlorides of Potassium and Calcium. By J. DRECKER (*Ann. Phys. Chem.* [2], **34**, 952—970).—It is found that in general the specific heat of a solution or mixture differs from the mean calculated from the specific heats of the constituents. This might be due to a difference in the internal work of expansion in the mixture and in the separate constituents, but if this were the only cause the observed specific heat at constant volume would agree with the value calculated from the specific heats of the constituents.

The author, in his previous investigations (*Ann. Phys. Chem.* [2], **20**, 870), found that for a large number of liquids the observed and calculated specific heats at constant volume agreed more closely than those at constant pressure.

The whole of the observed differences, however, cannot be explained by differences in the internal work of expansion.

The present paper contains an account of similar experiments made with solutions of the chlorides of potassium and of calcium of different concentrations.

The author finds that the compressibility of these solutions is less

than that of water, but the diminution is not proportional to the quantity of salt in solution. Up to a certain concentration, the compressibility increases with the temperature, as in the case of water, and afterwards it diminishes as in the case of alcohol, ether, chloroform, and other liquids. The concentration for which the compressibility is independent of the temperature is about 16 per cent. for potassium chloride and 20 per cent. for calcium chloride.

He confirms Braun's result (Abstr., 1887, 436), that the strength of a saturated solution of a salt depends on the temperature, but finds that Röntgen and Schneider's equation (*Ann. Phys. Chem.* [2], 29, 165) for determining the compressibility of a solid salt from that of its solution is only a very rough approximation.

The specific heats of the solutions, both at constant pressure and constant temperature, were found to be less than those of water when the solutions were dilute, and the differences increased with the concentration up to a certain amount, when they reached a maximum, and decreased with further concentration until, with sufficiently concentrated solutions, the specific heat was greater than that of water.

The differences between the observed specific heats and their calculated values were greater at constant volume than at constant pressure, showing that the internal work of expansion of the solutions is greater than that of the constituents, so that the behaviour of the solutions is in this respect exactly the opposite to that of the mixtures of liquids formerly investigated.

G. W. T.

Heat of Formation of Mercury Compounds. By J. THOMSEN (*Zeit. physikal. Chem.*, 2, 21—22).—Ostwald has pointed out that the reduction of mercurous nitrate by sulphurous acid, resulting in the separation of metallic mercury, the reaction by which the author formerly determined the heat of formation of mercurous oxide, does not take place with the assumed regularity, and that consequently the thermal data based on the above determination contain a constant error from this source. In order to obtain some idea of the magnitude of this error, the author has determined the heat evolved when mercurous nitrate is decomposed by a solution of iodine in potassium iodide resulting in the formation of mercury potassium iodide, and also when it is decomposed by potassium iodide alone, resulting in the separation of one-half of the mercury in the metallic state, and the conversion of the other half into mercury potassium iodide, the difference between these two reactions conducted under similar conditions being the heat evolved by the reaction $\text{HgI}_2, n\text{KIAq}$. Thus determined and calculated for one molecule of mercurous nitrate this quantity is 29090 cal., and as the former determination by means of the reduction experiment gave 37760 cal., the constant error of this latter method would appear to be 8670 cal. On this assumption, the corrected heats of formation of the following compounds would be:—

Hg, Cl ₂	54490 cal.	Hg ₂ , Cl ₂	65210 cal.
Hg, Br ₂	41880 „	Hg ₂ , Br ₂	50950 „
Hg, I ₂	25640 „	Hg ₂ , I ₂	31100 „
Hg, O	22000 „	Hg ₂ , O	24860 „
Hg, S	8220 „	Hg, Cy ₂	10280 „

H. C.

Heat of Formation of Mercury Compounds. By W. NERNST (*Zeit. physikal. Chem.*, **2**, 23—28).—The author has determined directly the heat of formation of mercuric bromide from liquid mercury at about 15°, and finds it to be 40460 cal. per gram-molecule, the number calculated by Thomsen from the reduction of mercurous nitrate by sulphurous acid (preceding Abstract) being 50600 cal. Taking the finely divided mercury obtained in the latter reaction and substituting it for the liquid mercury before used, a number about 12 per cent. higher was in fact obtained, but on examination, after repeated washings, the mercury was found still to contain nitric and sulphuric acids. This, together with the fact that in the finely divided state the mercury is already in a condition which favours the reaction, will perhaps serve to explain the discrepancy.

By means of the number obtained for mercuric bromide, the following heats of formation have been recalculated from Thomsen's numbers:—

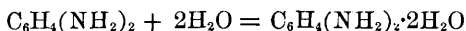
Hg, Cl ₂	53200 cal.		Hg ₂ , Cl ₂	62600 cal.
Hg, I ₂	24300 „		Hg ₂ , I ₂	28400 „
Hg, O	20700 „		Hg ₂ , O	22200 „

The heat of formation of mercuric from mercurous bromide was directly observed to be 16000 cal., and this would give for the heat of formation of mercurous bromide 24500 cal. By means of these new numbers the calculated E.M.F. of various galvanic elements containing mercury as one pole, is brought into agreement with the observed values, which has hitherto not been the case, using the numbers obtained from Thomsen's determination.

The heat of formation of cadmium bromide in aqueous solution was also determined and found to be 76300 cal., Thomsen's number, obtained by totally different method, being 75600 cal. H. C.

Heat of Formation of Salts of Phenylenediamine. By L. VIGNON (*Compt. rend.*, **106**, 1671—1674).—Paraphenylenediamine crystallises from a boiling saturated aqueous solution in transparent, white, monoclinic lamellæ which contain 2 mols. H₂O, melt at 80°, effloresce in a vacuum, and become rose-coloured when exposed to air. The normal sulphate, C₆H₄(NH₂)₂.H₂SO₄, forms micaceous plates and is only slightly soluble in water, the solution being acid to litmus. The oxalate also forms anhydrous crystals which do not melt and are very slightly soluble in water, the solution being acid to litmus.

Heat of solution of anhydrous paraphenylenediamine —3·8 Cal., of the hydrate —7·4 Cal., whence



develops +3·6 Cal.

The other values obtained were as follows:—

C ₆ H ₄ (NH ₂) ₂ diss. + HCl dil.	develops	+8·8 Cal.
C ₆ H ₄ (NH ₂) ₂ diss. + 2HCl dil.	„	+14·7 „

$C_6H_4(NH_2)_2$ diss. + $\frac{1}{2}H_2SO_4$ dil.	develops	+9.6 Cal.
$C_6H_4(NH_2)_2$ diss. + H_2SO_4 dil.	"	+19.2* "
$C_6H_4(NH_2)_2$ diss. + AcOH dil.	"	+7.2 "
$C_6H_4(NH_2)_2$ diss. + 2AcOH dil.	"	+8.4 "
$C_6H_4(NH_2)_2$ diss. + $\frac{1}{2}H_2CO_3$ dil.	"	+8.8 "
$C_6H_4(NH_2)_2$ diss. + H_2CO_3 dil.	"	+22.2 "

It is evident that the neutralisation of one of the basic functions of paraphenylenediamine reduces the intensity of the remaining function. So far at least as the first function is concerned, paraphenylenediamine is a more energetic base than aniline. C. H. B.

Heat of Neutralisation of Aromatic Amines. By L. VIGNON (*Compt. rend.*, 106, 1722—1724).—The following results were obtained:—

	Hydrochloric acid.	Sulphuric acid.	Acetic acid.
Aniline, 1st equivalent	7.38	8.75	3.85
" 2nd "	0.92	0.71	2.14
Methylaniline, 1st equivalent	6.91	8.06	—
" 2nd "	1.31	0.92	—
Dimethylaniline, 1st equivalent.....	6.81	7.60	—
Dimethylaniline, 2nd equivalent.....	1.02	0.71	—

The quantity of heat developed by the successive action of one and two equivalents of acid on the amines affords a measure of the heats of formation of the different salts and also a measure of the degree to which the salts are dissociated in dilute solution. With aniline and acetic acid the action is far from complete. A comparison of the anilines with ammonia and the methylamines shows that the substitution of methyl for hydrogen in ammonia or in the NH_2 group in aniline has little effect on the energy of the basic function, whereas the substitution of phenyl for hydrogen in ammonia very considerably reduces the activity of this function. C. H. B.

Heats of Combustion of Organic Compounds. By F. STOHMANN (*Zeit. physikal. Chem.*, 2, 29—35; comp. Abstr., 1887, 878, 1011).—Contains the tabulated results of the author's published experiments on the above, giving the heat of combustion per gram and per gram-molecule of each substance, and the heat of formation calculated from this, using Berthelot's numbers, $C = 94$ Cal. and $H_2 = 69$ Cal. H. C.

Thermo-chemistry of Nitrogen-derivatives of Benzene. By P. PETIT (*Compt. rend.*, 106, 1668—1669).—The heats of combustion were determined by means of the calorimetric bomb, and are given in the following table, in which A is the heat of combustion per gram-molecule at constant volume, B the corresponding value under constant pressure, and C the heat of formation from the diamond, hydrogen, and nitrogen.

* Crystallised.

	A.	B.	C.
Azoxybenzene	1529.55	1530.6	-57.6 Cal
Azobenzene	1555.0	1556.4	-83.4 „
Hydrazobenzene ..	1598.0	1599.6	-57.6 „
Phenylhydrazine ..	805.24	806.3	+33.7 „

The formation of azobenzene from aniline and nitrosobenzene, C_6H_7N liq. + C_6H_5 liq. + HNO_2 dil. = $C_{12}H_{10}N_2$ + $2H_2O$ liq., develops +42.3 Cal. The formation of phenylhydrazine from aniline and hydroxylamine, C_6H_7N liq. + NH_2OH dil. = $C_6H_8N_2$ + H_2O , develops +96.7 Cal.; the formation of phenylhydrazine hydrochloride, $C_6H_8N_2$ liq. + HCl dil. = $C_6H_8N_2 \cdot HCl$ diss., develops +8.9 Cal.; the heat of dissolution of the hydrochloride is -5.96 Cal., and hence $C_6H_8N_2$ liq. + HCl gas = $C_6H_8N_2 \cdot HCl$ solid, develops +32.2 Cal., a value which approaches the heat of formation of ammonium chloride by the corresponding reaction. C. H. B.

Disintegration of Glowing Platinum. By H. KAYSER (*Ann. Phys. Chem.* [2], **34**, 607—608).—In some determinations of the tension coefficient of air as a function of the pressure, which the author had been making, he passed the air through a glass tube containing platinum wires heated to redness in order to remove traces of hydrocarbons. He found that the result was to considerably increase the tension coefficient, which however returned to its normal value when the air was allowed to stand for some time after passing over the heated platinum.

He concluded that the phenomenon was due to the presence of disintegrated particles of platinum, and the conclusion was confirmed by the fact that the tension coefficient immediately returned to its normal value when the air was filtered by being forced under pressure through very tightly packed cotton-wool. G. W. T.

Viscosity of Gases at High Temperatures, and the Pyrometric Use of the Principle of Viscosity. By C. BARUS (*Amer. J. Sci.*, **35**, 407—410).—By passing gases under known conditions through capillary platinum tubes maintained at known temperatures varying from 5° to 1400°, the author has obtained a series of data for determining the relation existing between the viscosity of a gas and its temperature.

The results obtained show that for the range of temperature within which the observations were made, the mean increase in the viscosity of a gas is proportional to $T^{\frac{1}{3}}$, where T is the absolute temperature, and taking into account the relations established by Clausius and Maxwell, it is found that the mean free path of a molecule of a perfect gas varies directly as the sixth root of the absolute temperature, a result of considerable importance, as the condition that the length of the mean free path should be independent of the temperature is usually regarded as a criterion of a perfect gas.

If this law of the sixth root is assumed as the criterion of a perfect gas, namely, one in which no transient mechanically cohering molecular aggregates are formed, it follows that the mean free path must be proportional to the cube root of the velocity of the mean square.

If the exact law of thermal variation of the viscosity of a gas were known, Poiseuille-Meyer's equation applied to transpiration data would give us a means of measuring temperature absolutely over a wider range, and with an accuracy hitherto unattainable. The author suggests that the method may be advantageously applied to the study of the phenomena of gaseous dissociation, of phenomena at temperatures in the neighbourhood of the critical temperature, and for the determination of vapour-pressure at high temperatures.

G. W. T.

Change of Volume in Gases on Mixture: Is the Pressure of a Saturated Vapour Independent of the Presence of other Gases? By F. BRAUN (*Ann. Phys. Chem.* [2], 34, 943—952).—

The question whether the presence of a saturated vapour is the same in a vacuum as in the presence of a gas is still a disputed one. Regnault attributed the differences observed by him to secondary causes, such as the deposition of condensed vapour on the walls of the containing vessel.

The author describes a series of careful experiments on sulphurous anhydride, from the results of which he arrives at the conclusion that the pressure of this vapour at the temperature of condensation is diminished by at least 3.9 mm. of mercury by the addition of an equal volume of carbonic anhydride at the same pressure and temperature, and by 1.3 mm. by the addition of an equal volume of nitrogen under similar circumstances. He infers in general that the pressure of a saturated vapour is not the same in the presence of a gas as in a vacuum, even when all disturbing causes are absent.

The question is of importance in relation to the dissociation of gases, and up to the present it has not been found possible to decide it on theoretical grounds.

G. W. T.

Determination of the Specific Weight and Vapour-pressure of Mixtures of Sulphurous and Carbonic Anhydrides.—By R. PICTET (*Ann. Phys. Chem.*, [2], 34, 734—736).—The author states that in a work in the press on "Machines for Freezing by Compression," he has criticised at length the results given in A. Blumcke's paper (this vol., p. 775), and in the meantime he calls attention to the following points:—

(1.) In his earlier work on the subject, he has pointed out that no satisfactory determination has yet been made of the chemical constitution of a liquid boiling at -19° , and that the formula SCO_4 , analogous to SO_3H_2 , must only be looked on as a label adopted for convenience.

(2.) The principal result of his investigations consisted in the establishment of the fact that the mobile liquid boiling at -19° has at 30° a vapour-pressure of only 4.5 atmospheres instead of 8, as theory would lead us to expect.

(3.) Blumcke found this vapour-pressure to be 4.6 instead of 4.5, a smaller difference than that existing between different determinations of Regnault's.

(4.) Blumcke's results were obtained by means of Cailletet's apparatus, and during the compression and liquefaction of the gas

its volume was reduced to 1/300 or 1/400 of its original value, so that the slightest trace of a foreign gas would be sufficient to introduce an error of two or three atmospheres, and he considers that this is the source of the errors which Blumcke thought he had found.

(5.) Blumcke's own determinations of the vapour-pressure of sulphurous acid differed by from 0.18 to 0.92 of an atmosphere from those obtained by Regnault, and he thinks that Blumcke has not given sufficient weight to these deviations. G. W. T.

Determination of Vapour-pressure from the Rate of Evaporation. By W. MÜLLER-ERZBACH (*Ann. Phys. Chem.* [2], **34**, 1047—1048).—The author observes that G. Tammann (this vol., p. 403) had made some determinations of the vapour-pressure of aqueous solutions by measuring the quantity of water absorbed by a stream of dry air, a method which he had himself employed, and in agreement with his own results, finds that the values so obtained agree with those obtained by the barometric method. Tammann, however, regards the author's determinations of the vapour-pressure of solids containing combined water as inaccurate, but without giving any experimental results in support of his conclusion.

Reserving a more detailed reply to Tammann's criticism, the author makes the following observations:—

(1.) The vapour-density d_1 of the uncombined water is given by the known formula of Stefan, $d_1 = c/l \log p/(p - p_1)$, where c is the coefficient of diffusion, and l the length of the open tube. It follows that approximately $d_1 l/c = 2p_1 M/(2p - p_1)$, and for the combined water $d_2 l/c = 2p_2 M/(2p - p_2)$, or $d_1/d_2 = p_1/p_2$, since $(2p - p_2)/(2p - p_1)$ is nearly equal to unity. Assuming the diffusion to be proportional to the vapour-pressure directly, and to the square of the absolute temperature, this relation is obtained still more directly.

(2.) The author's method of observation determines the constant pressure during dissociation, whilst the statical method gives the final pressure resulting from the dissociation. The method employed by Tammann approximates to the latter when the current of air is slow.

(3.) The author's results agree well together, and warrant the conclusion that the dissociation pressure is constant for a given salt.

(4.) The values obtained for the vapour-pressure vary according to the nature of the salt, by evaporation of part of the water of crystallisation, and by long exposure to the air, which even when there is no sensible evaporation makes the salt much more readily decomposable.

(5.) In the case of chrome alum and copper sulphate, the author has confirmed the values obtained for the vapour-pressure by direct observations on the atmosphere in contact with the salt.

G. W. T.

Some Properties of Solutions. By P. DUHEM (*J. de Phys.* [2], **7**, 5—25).—In his treatise "Le Potential Thermodynamique et ses Applications," the author deduced from the researches of Malaguti and of Berthelot, a proposition with regard to the thermodynamic potential Φ , of a solution containing a mass m_0 of solvent and m_1, m_2 ,

of different substances in solution, a relation which in the case of only two substances in solution is represented by the equation—

$$\frac{d^2\Phi}{dm_1dm_0} = \frac{d^2\Phi}{dm_2dm_0},$$

but further investigation has shown that this law is not in agreement with experiment.

The author defines a series of substances 1, 2, &c., of molecular weights w_1, w_2 , &c., as belonging to the same series relative to a solvent, provided that when masses m_1, m_2 are dissolved in a mass m_0 of the solution, the equation—

$$w_1 \frac{d^2\Phi}{dm_1dm_0} = w_2 \frac{d^2\Phi}{dm_2dm_0},$$

holds good, and he finds from experiment, that all the substances which are soluble in a given solvent can be arranged in a small number of such series. The function $d\Phi/dm_n$ the author calls the thermodynamic potential function of the substance n within the solution. It is then shown to follow very simply that the potential function of the solvent is unaffected by replacing a given weight of one of the substances in solution by an equivalent weight of another substance of the same series. As an important special case of this we have the proposition that if n solutions are formed with the solvent, each containing one of the substances 1, 2, . . . n , belonging to the same series with respect to the solvent, the potential function of the solvent will have the same value in each of the solutions, provided their concentrations are in the proportion of the molecular weights of the substances in solution.

Now it is shown in the author's paper on osmotic pressure (this vol., p. 1022) that on approximation to the point at which the compressibility of water may be neglected, the osmotic pressure expressed in terms of a column of water at the temperature of observation, measures the difference, at this temperature, between the potential function of pure water and that of the water within the solution, each being taken at the pressure in the solution. It follows, therefore, that all the n solutions of the preceding paragraph will be isotonic.

It is then shown that these solutions will have the same solidifying point, a statement which sums up the extensive series of experimental results obtained by Raoult (Abstr., 1880, 523; 1882, 1260; 1883, 7, 278, 952; 1884, 254, 701, 808, 952, 1248.)

The author shows that the remarkable relation between the lowering of the solidifying point of water by dissolving an acid or a base in it, and the energy of the acid or base, first deduced experimentally by Raoult, is to be expected from theoretical considerations.

Kirchhoff ("Ueber einen Satz der mechanischen Wärmetheorie, &c.," *Ann. Phys. Chem.*, 103), bases his discussion of the properties of gaseous solutions on the three hypotheses: (1) that the gas obeys Boyle's and Gay-Lussac's (Charles's) laws; (2) that the solution of the gas in the liquid does not alter the vapour-pressure of the latter; (3) that the volume of gas dissolved, measured at the final pressure, is at any given temperature in a constant ratio to the volume of the

liquid. The author shows that the second hypothesis is a necessary consequence of the first and third. He then shows that all slightly soluble gases satisfying (1) and (3) belong to the same series, and that for all gases of this kind and other substances belonging to the same series—

$$\frac{\Pi}{s} = \frac{RT}{w_1},$$

where s is the concentration or ratio of mass of dissolved substance to mass of solvent, w_1 the molecular weight of the former, T the temperature, and Π the osmotic pressure of the solution expressed in terms of a column of the solvent.

This law, the form of which recalls the general formula including the laws of Boyle, Gay-Lussac (or Charles), and Avogadro, is the one given by Vant' Hoff as being applicable to the majority of substances in sufficiently dilute solutions.

The author further finds that for solutions of gases obeying the conditions (1) and (3), there is absolutely no disengagement of heat due to dilution or to solution of the gas.

In general, where $\lambda_1 m_1$ is the quantity of heat produced by the solution of the mass m_1 of gas, s the concentration of the saturated solution of gas at temperature T , α the coefficient of solubility, namely, the ratio of the volume of the gas to that of the liquid, w_1 the molecular weight of the gas, J the mechanical equivalent of heat, the author obtains the relation—

$$\lambda_1 = -\frac{JRT^2}{w_1} \frac{d}{dT} \log S,$$

which may be transformed by considering properties of gases, to—

$$\lambda_1 = \frac{JR}{w_1 T} \left(1 - T \frac{d \log \alpha}{dT} \right),$$

which is the same as that arrived at by Kirchhoff in the memoir previously referred to.

Similar reasoning may be applied to the case of solutions of salts belonging to the same series as the gases considered, which Raoult and Vant' Hoff call the normal series, giving the results:—

(1.) The dilution of a solution of a substance belonging to the normal series gives rise to no production or loss of heat.

(2.) The heat of solution of any substance belonging to the normal series is independent of the concentration of the solution, and is given by the formula—

$$\lambda_1 = -\frac{JRT^2}{w_1} \frac{d}{dT} \log S,$$

where S is the solubility of the salt at the temperature T , and w_1 its molecular weight.

This law had been given previously by Le Chatelier (Abstr., 1885, 340, 473), as a general formula for heat of solution. The present investigation shows that it is only applicable to substances belonging to the normal series.

G. W. T.

Theory of Liquids. By D. KONOWALOFF (*Zeit. physikal. Chem.*, **2**, 1—5).—In a former communication (*Zeit. physikal. Chem.*, **1**, 39), the author showed that if the expansion by heat of a liquid follow the law $v = 1/(1 - kt)$, the alteration in the compressibility with temperature would be expressed by $\phi = \phi_0 T/T_0(1 - kt)^3$. Calculations with this formula by Grimaldi for ether, pentane, and chloroform at 100°, led to values of ϕ totally different from those observed, but it is here shown that this was owing to an error in the calculation, and that whereas in the case of ether and pentane there is certainly a considerable difference between the calculated and observed values, in that of chloroform the two are in close agreement. The explanation of the exception exhibited by ether and pentane is that at a temperature so far above their boiling points the relation $v = 1/(1 - kt)$ no longer holds. The author shows that it may be replaced by $v = (1 - k_2t)(1 - 2k_2t)$ from which $\phi = \phi_0 T(1 - k_2t)/T_0(1 - 2k_2t)^3$, which formula gives values for ϕ for ether and pentane at 100° in close agreement with those observed. H. C.

Attempt to eliminate the Influence of the Change in the Volume of the Vessel when measuring the Compressibility of Liquids. By J. J. BOGUSKI (*Zeit. physikal. Chem.*, **2**, 120—123).—The principle of the method used is to measure the volume of the liquid in compression and in its normal condition, not as usually occurs in one and the same vessel, but in two different vessels. The apparatus described admits of the above being carried out, and a measurement gave for the true compressibility of ether at 19.2° 0.00018346 per atmosphere. H. C.

Compressibility of Sylvin, Rock-salt, and Aqueous Solutions of Potassium Chloride. By W. C. RÖNTGEN and J. SCHNEIDER (*Ann. Phys. Chem.* [2], **34**, 531—551).—In this paper the authors tabulate the results of a large number of experiments in continuation of their researches on compressibility. In a former paper (this vol., p. 22), the authors obtained the value 0.049 for the relative apparent compressibility of rock-salt at 17.9°. They now find by experiments carried out with greater accuracy, that its value is 0.0477 at 18.4°, and that a more exact determination of the content of the piezometer and of the density of the rock-salt used in the former experiments gives the number 0.0475 as the corrected result, and this is in close agreement with the more recent determination. Taking 0.0476 as the value at 18°, and multiplying by 0.000044 Atm.⁻¹, the value obtained for the apparent compressibility of water, they obtain for the apparent compressibility of rock-salt the value 0.00000210 Atm.⁻¹.

Experiments on powdered rock-salt and powdered sodium chloride show that the compressibility of the powder is slightly greater than that of the solid salt.

For the apparent compressibility of a concentrated solution of commercial chloride of sodium at 18.4° they obtain the value 0.00000284 Atm.⁻¹, and for solid sylvin at 18° they obtain the value 0.00000424 Atm.⁻¹. The difference between the values of the com-

pressibility of rock-salt and sylvin is a good deal larger than would result from Voigt's researches (*Berl. Ber.*, 1883, 971); his values, however, were not determined directly, but involved certain assumptions of Poisson's with respect to the theory of elasticity.

In a former paper (*Ann. Phys. Chem.* [2], 29, 193), the authors found that the observations could be represented by the formula $(y - b)(n + a) = (1 - b)a$, where a and b are constants, y the relative apparent compressibility, and n the number of molecules.

If this formula held good for $n = \infty$, we should have $y = b$ as the relative apparent compressibility of the solid salt. In the case of sodium chloride, the results obtained in this manner agree well with the direct determinations, but this is not the case for potassium chloride.

The authors merely publish the results obtained in this paper as an instalment of an extensive series which they hope will ultimately throw some light on the nature of solutions. G. W. T.

Theory of Solution. By W. OSTWALD (*Zeit. physikal. Chem.*, 2, 36—37).—The analogy which Van't Hoff has drawn between a substance in the gaseous state and the same in solution, and the hypothesis of Arrhenius (this vol., p. 896) that substances in dilute solution undergo dissociation into their ions, may be tested by the application of gaseous laws to the state of solution. Such a law is that for dissociation at constant temperature, where neither of the products of decomposition is present in excess, $p/p_1^2 = c$, where p is the pressure of the undecomposed, p_1 that of the decomposed portion, and c a constant. Since pressure in solution is proportional to the amounts u and u_1 of substances present and inversely to the volume, we have $uv/u_1^2 = c$. But u and u_1 may be calculated from the electrical conductivity as Arrhenius has shown. If u_v is the conductivity for volume v of an electrolyte, and μ_∞ the limiting value of the same for infinite dilution, then $u/u_1 = (\mu_\infty - \mu_v)/\mu_v$, since the conductivity μ_v is proportional to the dissociated amount of the electrolyte u_1 . Hence for all binary electrolytes we have as the law of dilution $(\mu_\infty - \mu_v)v/\mu_v^2 = \text{const.}$

The author proposes to subject this theory to further investigation.

H. C.

Hydrates of Gases. By VILLARD (*Compt. rend.*, 106, 1602—1603).—The gases were introduced, together with a small quantity of water, into the tube of a Cailletet's apparatus, compressed, released suddenly, and again compressed, or simply compressed, the tube being cooled below 0°. The latter method was found to be sufficient; the sudden release of pressure only promotes the formation of the hydrates by producing small quantities of ice. So long as the pressure is maintained the hydrates are stable, provided the temperature does not exceed a certain limit, but if the pressure is removed the hydrates decompose with effervescence. On restoring the pressure, the hydrates are again formed on the sides of the tube owing to the moisture having been deposited thereon. The tension of dissociation of several hydrates was determined.

Methane.—This hydrate is formed at -2° to -3° under a pressure

of 30 atmos. Tension of dissociation 27 atmos. at 0° , 200 atmos. at 19° . Above 21° the hydrate decomposes even under a pressure of 300 atmos.

Ethane.—6 atmos. at 0° , 28 atmos. at 12° , above which it decomposes under any pressure.

Acetylene.—7 atmos. at 0° , 34 atmos. at 14° .

Nitrous oxide.—10 atmos. at 0° , 43 atmos. at 12° , above which it decomposes under any pressure.

Hydrates of gases have a critical temperature of decomposition above which they cannot exist under any pressure. Some gases, such as methane or ethane, form crystalline hydrates at temperatures above their points of liquefaction, and the critical temperature of the hydrate is higher than the critical temperature of the gas.

Nitrogen, oxygen, carbonic oxide, nitric oxide, cyanogen, ammonia, propylene, butylene, and allylene do not yield crystalline hydrates under the conditions described.

C. H. B.

Hypothesis of Dissociation of Salts in very Dilute Solutions. By E. WIEDEMANN (*Zeit. physikal. Chem.*, **2**, 241—242).—The author criticises the results obtained by Arrhenius and Planck (this vol., pp. 895, 896). The exceptions to the law of the reduction of the freezing point E in water, which is of the form $E = \text{const. } n_1/n$, where n_1 is the number of molecules of the dissolved substance and n that of the solvent, are explained by Planck as arising from the increase in n_1 due to dissociation of the salt molecules, but would equally result from a decrease of n caused by aggregation of the molecules of the solvent at the freezing point. The simplest explanation of the maximum density and expansion of water between 4° and 0° is that the water already contains in a process of formation solid producing ice molecules, so that at the freezing point the salt is no longer in the presence of simple water molecules but of water and ice molecules, and n thus decreasing in value has the same effect on E as an increase in n_1 , which, however, remains the same. The anomalous position occupied by water among liquids in respect of density explains the occurrence of exceptions with this solvent to the law of the reduction of the freezing point and not with others. Hence, while still admitting the possibility of a partial dissociation of some salts of weak acids and bases in solution, the above exceptions should be regarded as due in the majority of instances to the behaviour of the solvent and not to that of the salt. Arrhenius looks on the properties of many compounds in solution being of a so-called additive nature, that is, they may be represented as the sum of the properties of the atoms, as strong presumptive evidence of dissociation, but additive properties occur equally in solids, the molecular heat being the sum of the atomic heats, the molecular volume the sum of the atomic volumes, and so on. Those proofs also which are deduced from the electrical conductivity must be considered as unsatisfactory, so little being known at present of the apparently complicated laws by which this process is regulated.

Ostwald, in a note on the above, raises the objection to Wiedemann's assumption with regard to the reduction of the freezing point, that unless it underwent a polymerisation simultaneous and exactly

proportional to that of the solvent, no salt could behave in a normal manner in water, as it is well known that all non-electrolytes do. He points out that Arrhenius has not advanced the view that a compound having additive properties is a sign of dissociation, but only that if substances are dissociated that will have additive properties similar to those which hold for salts in dilute solution. He further maintains that the explanations afforded by the new hypothesis itself serve in great measure to throw light on the nature of the electrical conductivity of solutions, and remove the complications to which Wiedemann alludes.

H. C.

Dissociation of some Alums and of Sodium Acetate. By W. MÜLLER-ERZBACH (*Ber.*, 21, 2222—2224).—Potash alum loses 8 mols. H_2O at 44.8° under a constant tension of 0.14, 1 mol. H_2O is given off at 44.2 under a somewhat less constant tension of 0.02 to 0.03, and 3 mols. remain, so that there are certainly two and probably three different degrees of force with which the water is held in combination. Ammonium alum behaves similarly, 8 mols. H_2O are evolved at 41.3° under a tension of 0.11, and 1 mol. H_2O at 45.8 under a tension of 0.016.

Soda alum and chrome alum lose only half of their water under a considerable tension which, for soda alum is 0.88 at 30.5° and for chrome alum 0.49 at 27.8° . With freshly crystallised soda alum at 18.5° , the tension remained 0.05 for two days, rose on the third day to 0.81 at 28.8° , and after that was normal and remained so even at a lower temperature.

Sodium acetate loses all its water at 29.8 under a constant tension of 0.31.

F. S. K.

Osmotic Pressure. By P. DUHEM (*J. de Phys.* [2], 6, 397—414).—In a previous memoir in the same volume, the author arrived at some conclusions apparently at variance with those of Van't Hoff (this vol., p. 778), but he now points out that this was due to his having attributed a different meaning to the term osmotic pressure.

When an aqueous solution of salt is separated from pure water by a diaphragm permeable to water but not to the salt, there will be a difference of pressure on opposite sides of the diaphragm when the condition of equilibrium, in which there is no flow of water through the diaphragm, is attained. This difference of pressure, which is a function of the concentration of the solution, Van't Hoff calls the osmotic pressure.

The author then proceeds to apply the theory of the thermodynamic potential to osmotic relations, and deduces some general results of considerable interest, more especially as they confirm a number of conclusions at which Van't Hoff arrived experimentally. He shows that in order to maintain a given solution in osmotic equilibrium with pure water at the pressure p , a pressure p' must be applied to it, depending on p , on the temperature, on the nature of the salt, and on the concentration of the solution, but independent of the shape of the containing vessel, or of the form and material of the diaphragm.

Adopting Willard Gibbs's definitions of the potential function of

pure water and of the salt in the solution, he finds that the pressure p' is the pressure at which the potential function of the water in the solution becomes equal to the potential function of pure water at the pressure p . Both these propositions were formulated by Van't Hoff, and are now shown to follow rigorously from the laws of thermodynamics.

The pressure p' is shown to be necessarily greater than the pressure p , and it must increase with the concentration.

If the compressibility of water is neglected, it is shown that to this approximation the osmotic pressure expressed in terms of a column of water at the temperature of observation, measures the difference, at this temperature, between the potential function of pure water and that of the water within the solution, each being taken at the pressure in the solution.

When two solutions of different salts and of different concentration are in osmotic equilibrium with water at the same pressure p , while the solutions are subject to the same pressure p' , Van't Hoff calls them isotonic. The author obtains an expression by means of which, when the vapour-pressure of a solution is known, and also the law of the compressibility of water-vapour, the vapour-pressure of an isotonic solution can be determined. Assuming the laws of Boyle and Gay-Lussac to be applicable to water-vapour, and neglecting the specific volume of the solution in comparison with the specific volume of its vapour, the author arrives at the result that two isotonic solutions at the same temperature have approximately equal vapour-pressures.

Van't Hoff states the theorem as an exact one, but the conditions of his experiments were such that the pressure p' , at which the solutions are isotonic, was equal to the vapour-pressure P of one of them, and the formulæ in the present paper will then give P equal to P_1 , the vapour-pressure of the other solution.

The author shows that the difference in the solidifying points of two isotonic solutions under any given pressure is exceedingly small. Van't Hoff enunciates this law in an exact but more restricted form, viz., two isotonic solutions have the same solidifying point at the pressure for which they are isotonic, and the author's formulæ show this to be rigorously true.

For the relation between the osmotic pressure $\pi = p' - p$, and the temperature T , Van't Hoff gives $d\pi/dT - \pi/T = 0$, but this the author shows to be incorrect, the true relation being of a much more complicated character, and not approximating to this even when, as Van't Hoff supposes, the solutions are so dilute that the further dilution produces no calorific effects.

G. W. T.

Permeability of Vegetable Membranes for Air. By E. LIETZ-MANN (*Bied. Centr.*, 1888, 497).—Cork lamellæ, even when there is a great difference of pressure, are impermeable for gases, whilst the tender cellular membrane of the leaves of *Peperomia magnolifolia*, and also the *cuticula* in a saturated state, are permeable to air. Air permeates more readily through a saturated than through an air-dry membrane. The membranes of woody tissue are also very readily

permeated, and the more so if they be moist. Experimenting with bladder, the author finds that animal membranes follow the same law as vegetable.

E. W. P.

Equilibrium in the Retention of Water by Dilute Sulphuric Acid and Hydrated Salts. By W. MÜLLER-ERZBACH (*Zeit. physikal. Chem.*, 2, 113—119).—Two salts were experimented with, sodium dithionate and lead acetate. In each case water passes from the salt to sulphuric acid of a tension that is slightly lower, but the reversal of the change and the passage of water from the acid to the salt requires that the tension of the acid should be considerably higher than that of the salt. This is independent of the state of aggregation of the salt. Experiments were made towards ascertaining the influence which slight impurities might have on the tension, but without definite results.

H. C.

Studies in Chemical Dynamics: Oxidation and Reduction Processes. By W. OSTWALD (*Zeit. physikal. Chem.*, 2, 127—147).—The author finds that the increase in the velocity of oxidation and reduction processes produced by the presence of free acids is in proportion to the constants of affinity of these latter. The increase in speed of the reactions $\text{HBrO}_3 + 6\text{HI} = \text{HBr} + 3\text{H}_2\text{O} + 6\text{I}$ and $2\text{CrO}_3 + 6\text{HI} = 2\text{Cr}(\text{OH})_3 + 3\text{I}_2$ in the presence of various acids was measured. A comparison with the constants of affinity and the electrical conductivities shows that the numbers representing this increase of speed for each acid are of the same order.

An exception in the first reaction was found for the case of chromic acid. The number for this is abnormally high, the explanation probably lying in a contact action of some sort occurring. That a recurring reduction and oxidation of the chromic acid does not take place is shown by the completely neutral action of chromium sulphate. An influence which may, however, be in some degree susceptible of the latter explanation is that of ferrous and ferric salts, both of which increase the speed of the reaction. In the case of ferrous salts the increase appears to be approximately inversely proportional to their molecular weights. A large number of chlorides were examined but were mostly indifferent, having no appreciable effect on the speed of the reaction. Manganese chloride increases the speed slightly, and cupric chloride very appreciably, but this latter oxidises the hydriodic acid. Cadmium chloride has a great effect in decreasing the speed, but this is owing to its decomposition by the hydriodic acid and consequent removal of the latter. The description of the behaviour of the chlorides applies equally to that of the bromides.

H. C.

Decomposition of Ammonium Salts by Bromine Water. By S. RAICH (*Zeit. physikal. Chem.*, 2, 124—126).—The decomposition of ammonia by bromine, $2\text{NH}_3 + 3\text{Br}_2 = \text{N}_2 + 6\text{HBr}$, takes place with very different velocities for ammonium salts and for free ammonia, being much slower with the former. As this would probably depend in some measure on the affinity coefficients of the acids, experiments were made to determine the relative velocities

of the reaction with different ammonium salts. The chloride, nitrate, sulphate, oxalate, acetate, tartrate, monochloracetate, formate, succinate, and malonate were taken in 1/20 normal solutions, and 12 c.c. of each titrated with 25 c.c. 3/40 normal bromine water at 25°. The results show that the velocity of the reaction is in some way connected with the affinity coefficients of the acids, as the stronger the acid which is combined with the ammonia the slower the reaction. In the case of the oxalate, formate, succinate, and malonate, the bromine attacks the acid as well as the ammonia, thus complicating the reaction. H. C.

Velocity of Etherification determined by means of Electrical Conductivity. By NEGREANO (*Compt. rend.*, 106, 1665—1668).—The rate of etherification of a mixture of ethyl alcohol and acetic acid was measured by determining the resistance of the liquid by Lippmann's method. The results were similar to those of previous observers, and the method is generally applicable. C. H. B.

Influence of Neutral Salts in Chemical Reactions. By J. SPOHR (*Zeit. physikal. Chem.*, 2, 194—217).—The author has continued his investigations on the influence of neutral salts on the inversion of cane-sugar (Abstr., 1885, 1181; 1886, 502) by studying the influence which the chlorides of potassium, sodium, lithium, magnesium, cadmium, mercury, calcium, strontium, barium, and manganese have on the rate of the inversion of cane-sugar by hydrochloric acid. This influence appears as before to be proportional to the amount of neutral salt present, and for salts belonging to the same series in the periodic system to decrease with rising molecular weight. The same amount of neutral salt with strong acid has approximately as much greater influence than with weak acid as the constant of inversion of the former is greater than that of the latter, so that the influence of any given quantity of neutral salt will decrease with the increasing dilution of the acid.

A study was also made of the influence of salts on the saponification of ethyl acetate by potassium hydroxide. From these and the above experiments the author draws the conclusion that the influence of the neutral salt is due to its taking part in the reaction, and explains how this may be assumed to occur on the Williamson-Clausius hypothesis of dissociation. H. C.

Freezing Mixtures containing Solid Carbonic Anhydride. By L. CAILLETET and E. COLARDEAU (*Compt. rend.*, 106, 1631—1634).—The temperatures were measured by means of a thermoelectric couple which had been graduated against a hydrogen thermometer.

Compressed or porous solid carbonic anhydride alone, under atmospheric pressure, gives a temperature of about -60° ; in a vacuum maintained by means of a pump and potash the temperature is -76° . A mixture of ether and solid carbonic anhydride has a temperature of -77° under ordinary pressure, and -103° in a vacuum. This mixture solidifies liquid carbonic anhydride.

When solid carbonic anhydride is added to ether, it at first disappears rapidly, not owing to volatilisation, but because it dissolves in the

ether. The ether remains transparent, but after some time bubbles of gaseous carbonic anhydride are given off. If further quantities of the anhydride are added, the liquid becomes saturated, and loses its transparency. The temperature gradually falls until it attains a minimum exactly at the point of saturation. Any further addition of the anhydride causes no further reduction of temperature, but the liquid becomes more and more turbid. It is evident that the effect of the ether is due to its solvent action on the carbonic anhydride. Other solvents producing low temperature with the anhydride are methyl chloride, -82° ; sulphurous anhydride, -82° ; amyl acetate, -78° ; phosphorus trichloride, -76° ; alcohol, -72° ; and ethylene chloride, -60° . The temperature of mixtures of carbonic anhydride with methyl chloride or sulphurous anhydride in a vacuum is so low that the solvent solidifies, and the temperature of the mass remains constant from this point. With methyl chloride the temperature obtained is -106° . A mixture of carbonic anhydride and chloroform becomes solid under ordinary pressure, and has a temperature of -77° .

C. H. B.

Configuration of the Molecule of Benzene. By F. HERRMANN (*Ber.*, **21**, 1949—1959).—The author states that the various possible positions in space of the atoms in the molecule of a hydrocarbon can be ascertained by simple geometric considerations without making any assumption as to the nature of the carbon-atom. This statement is discussed and explained with the aid of figures in the case of methane, hexamethylene, and benzene.

F. S. K.

The Air of Coal Mines. By T. G. NASMYTH (*Brit. Med. Journ.*, **2**, 1888, 222—229).—The following is a summary of the results obtained from the physical, chemical, and biological observations made from a sanitary standpoint, on the air in coal mines.

The temperature was determined by wet and dry bulb thermometers, one set being placed above ground, the other below. Both were read daily for a period of three months, and the results are given in tables. The most noteworthy points were the uniform temperature of the mine from day to day, and the fact that the air was nearly always saturated. On 21 consecutive days, the temperature remained at 53° F.; the highest temperature in the mine was 55° F., the lowest, 53° F.

The volume of the air was measured by the anemometer, and tables are given showing the large volumes of air which are passed into mines.

Carbonic anhydride was estimated by Pettenkofer's method. In mines under 100 fathoms deep, the percentage in volumes was 0.181; in deep mines over 100 fathoms, it was 0.219.

Organic matter, estimated by Carnelley's method, showed a high result, expressed as oxygen needed for a million volumes of air, for shallow mines 30, and for deep 39. This high result is probably due to those various chemical substances which decolorise potassium permanganate, beside organic matter.

Oxygen was estimated by Franke's method. This method is not

strictly accurate, and the results are comparative. The estimation showed that when ventilation was deficient, oxygen was diminished.

Estimations were also made of ammonia and albuminoïd ammonia by Wanklyn's method.

In the biological experiments, Hesse's method for collecting and estimating the micro-organisms in air was employed. Some hundreds of microscopic preparations and cultivations were made, and for particulars the original report must be consulted. All varieties of microbes were found, the numbers not always being in relationship to the impurity of the air. Moulds preponderated. The presence of horses and men had always a distinct effect in increasing the numbers in Hesse's tubes. This method, though the best we have, is not exact, as it is impossible to be sure that all microbes are deposited on the nutrient jelly; and also a litre of air run out from the aspirator does not imply that a litre of air has passed into Hesse's tubes.

The general conclusion is drawn that the air of coal mines compares favourably with that of one-room houses, schools, and workshops. Miners are not unhealthy, and are not particularly affected by phthisis or bronchitis. These statements are supported by statistics.

W. D. H.

Inorganic Chemistry.

Molecular Weight of Sulphur, Phosphorus, Bromine, and Iodine in Solution. By E. PATERNÒ and R. NASINI (*Ber.*, **21**, 2153—2155).—The authors have made determinations of the molecular weight of sulphur, phosphorus, bromine, and iodine, by Raoult's method in a similar manner to that described (*Ber.*, **19**, 2527). Benzene was the solvent employed in the case of sulphur, and solutions of various concentration were experimented on. The coefficient of depression was constant, and the molecular formula was found to be S_6 . Aqueous and acetic acid solutions were employed for the determinations with bromine, and the results show that the molecular formula is Br_2 . The molecular formula of iodine was found to be I_2 , when very dilute solutions of benzene are employed, but in more concentrated solutions the results seem to indicate a greater complexity of the molecule. The molecular depression is constant in acetic acid solutions, and the results obtained point to molecular formula intermediate between I and I_2 . From the results obtained with phosphorus in benzene solution, it seems probable that it contains a mixture of molecules of P_4 and P_2 , but the sample employed was not quite pure.
F. S. K.

Molecular Weight of Sulphur. By H. BILTZ (*Ber.*, **21**, 2013—2017).—The author made determinations of the vapour-density of sulphur by Meyer's method, but obtained no constant results, although the apparatus was filled with pure nitrogen, and experiments with mercury gave fully concordant determinations. The cause of this

disagreement is the presence of an indifferent gas, and it was found that the larger the quantity of sulphur taken the higher were the results obtained.

Determinations made with Dumas' apparatus at 518° gave constant results, but the density gradually decreases as the temperature increases. At 467.9° the vapour-density is greater than that calculated for S_6 , and there is no fact which points to the existence of such a molecule. There is just as much ground for assuming the existence of molecules of S_5 , S_7 , S_2 , or S_n , as of S_6 .

The only results which are constant within a very considerable range of temperature are those which agree with the molecular formula S_2 .
F. S. K.

Remarks on the preceding Article. By V. MEYER (*Ber.*, **21**, 2018—2019).—The results obtained in the previous paper show clearly that in vapour-density determinations made by the author's method, the quantity of substance taken and the size of the bulb are without influence on the result only when the substance, at the temperature of the determination, is a normal gas, the density of which is not changed by pressure or temperature. In other cases, the results are dependent on the relative quantities of the substance and the gas (air or nitrogen) with which its vapour is mixed.
F. S. K.

Property of Carbon similar to that of Spongy Platinum. By G. A. HIRN (*Compt. rend.*, **106**, 1784—1785).—The author has noticed that a heated thread of carbonised lamp wick occasionally remained incandescent in a mixture of alcohol vapour with air.

C. H. B.

Absorption of Carbonic Oxide by Cuprous Chloride. By H. DREHSCHMIDT (*Ber.*, **21**, 2158—2164; compare this vol., p. 88).—A reply to Hempel (this vol., p. 556). A hydrochloric acid solution of cuprous chloride, free from carbonic oxide, and almost saturated with nitrogen by keeping it in an atmosphere of the latter, does not evolve gas when placed in contact with hydrogen, but the volume of hydrogen (89.71 parts) diminishes slightly (0.55 part). In a second and third experiment with the same volume of hydrogen, the diminution was 0.23 and 0.17 part respectively, and if the solution was now brought into contact with the same volume of nitrogen, the latter increased by 0.17 part.

When 92.95 parts of coal-gas, freed from carbonic anhydride, heavy hydrocarbons, and oxygen, is treated with 10 c.c. of a freshly prepared hydrochloric acid solution of cuprous chloride, and the process repeated five times, the loss of volume is 8.35, 1.63, 0.41, 0.27, and 0.03 parts respectively, the consecutive diminutions being due to absorption of carbonic oxide. Experiments in which carbonic oxide was absorbed by a solution of cuprous chloride, the solution then shaken with pure nitrogen, and the resulting gaseous mixture analysed, show clearly that the solution evolves carbonic oxide when placed in contact with nitrogen.
F. S. K.

Reactions Occurring in the Preparation of Water and Heating Gas. By J. LANG (*Zeit. physikal. Chem.*, **2**, 161—183).—The object in these investigations was to ascertain the nature of the reactions which occur at different temperatures between the gases produced by the action of steam on carbon and the limits of such reactions. The action of methane on carbonic anhydride sets in at about 700°, a partial reduction taking place, carbon being deposited, and carbon monoxide formed. Some of the carbon is due to the decomposition of the methane by heat which occurs at this temperature. Hydrogen is the chief product of the action of water-vapour on methane at about 1000°, arising both from the action of heat on the methane, and from the reaction between the two gases. The carbon from the methane gives a hard, bright deposit of graphite, which reduces the carbonic anhydride formed in this reaction but slowly even at 1000°, the carbon monoxide present being mostly due to the reduction of the dioxide by the methane. The action of oxygen on carbon results in the formation of carbonic anhydride alone if conducted at 500°, and not too rapidly. A rapid action causes local heating of the carbon and consequent reduction of a small portion of the dioxide to monoxide, which is also brought about by raising the temperature of the reaction. If oxygen mixed with carbon monoxide be passed over carbon, no change takes place in the monoxide at 500°, if the reaction takes place slowly, as the temperature is not high enough for its combustion, but the carbon is burnt to dioxide by the oxygen. If the stream of mixed gases be passed rapidly, the heat of the latter reaction raises the temperature, and combustion of the monoxide then takes place. These experiments show that in the combustion of carbon the formation of the monoxide is preceded by that of the dioxide. The action of water-vapour on carbon begins at about 600°. At this temperature carbonic anhydride and hydrogen are the sole products, but as the temperature rises carbon monoxide is also formed from the reduction of the dioxide. This is somewhat decreased in amount by the opposing action of the water-vapour, $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$, an effect which may be much reduced, though not entirely overcome, by having the carbon porous and present in quantity, offering a large surface for the quick removal of the water-vapour. The reduction of carbon dioxide to monoxide, the action of water-vapour on carbon monoxide, and the decomposition of water-vapour by carbon, can only take place within certain limits strictly defined by temperature, and at no temperature is any one of these reactions a complete one. H. C.

Lowest Oxide of Silver. By O. v. D. PFORDTEN (*Ber.*, **21**, 2288—2299).—The compound described as oxide (compare *Abstr.*, 1887, 699, and this vol., p. 221) must be regarded as a hydrate of silver, the composition of which is probably $\text{Ag}_4\text{H}_2\text{O}$ (? $\text{Ag}_4\text{H}\cdot\text{OH}$). The product which is first precipitated in the tartaric acid reaction (*loc. cit.*) is the hydrate, containing silver tartrate or sodium tartrate; it retains its impurities when washed with alcohol, alcoholic acetic acid, or solutions of different salts, and contains about 4 per cent. of water. The flocculent precipitate produced on adding alkali is

probably the pure hydrate, but it cannot be obtained in the dry state free from impurities; when washed with aqueous or alcoholic potash or ammonia, or with acetic acid, the organic impurities are removed, and a black powder is obtained which contains varying quantities of water, but always less than 4 per cent. Both preparations contain extremely small quantities of oxygen.

Silver hydrate is converted into metal when treated with hydrochloric acid, sulphuric acid, and most other acids, but phosphorous and sulphurous acid have no action in the cold. It is much more readily oxidised by potassium permanganate, potassium ferrocyanide, potassium dichromate, and iodine than metallic silver, and is decomposed into metal and water by cold, concentrated hydrogen peroxide, or when washed with water or solutions of salts. It loses its water slowly at 100°, but quickly at 110°.

All black compounds which are obtained by reducing solutions of silver probably consist of the hydrate.

F. S. K.

Solubility of Calcium Compounds. By A. H. ALLEN (*Chem. News*, 57, 236).—The author points out that the solubility of many calcium salts diminishes with an increase of temperature; such is the case, for example, with the acetate, the propionate, the normal valerate and butyrate, the iso-octate, the citrate, and the benzoate. This property, therefore, appears to be connected with the basic radicle as well as with the decomposition of unstable hydrates.

D. A. L.

Constitution of Hydraulic Cements. By H. LE CHATELIER (*Annales des Mines*, 1887, 345—404).—The author shows that when gypsum is subjected to a very regular and progressive rise of temperature, dehydration takes place in two stages; the first, at 120—130°, results in the loss of 1.5 mol. H_2O ; the second, at 160—170°, completes the dehydration. In confirmatory experiments, gypsum was exposed for prolonged periods to various fixed temperatures, and it was observed that even at 155° the dehydration did not extend beyond the first stage, whilst at 194° dehydration was complete. The decomposition is independent of pressure, but proceeds more or less rapidly according as the temperature is higher or lower. The product of the first stage, $2CaSO_4 \cdot H_2O$, may be obtained in long, rectangular prisms of extreme tenuity, by heating a saturated solution of calcium sulphate at 130—150° in sealed tubes, then to avoid rehydration, which takes place very rapidly in water below 130°, the tube is opened while hot, and the moist contents are thrown into absolute alcohol; the crystals obtained in this manner when dried at 100° have the above composition. The incrustation in boilers supplied with sea-water is an impure form of this compound. The author explains the setting of plaster, and bases his explanation on the hydration of the burnt gypsum in the presence of water, the formation of a supersaturated solution of normal sulphate, and the crystallisation of the latter salt; the water set free is then ready to attack a fresh portion of burnt gypsum, and so on until the whole mass has undergone conversion. Under these conditions, the sulphate crystallises abnormally, forming spherulitic

aggregations of filiform prisms ; favourable both for great adhesion and interlacing, as well as for the formation of a solid crystalline mass.

In support of this explanation the following experiment was made with anhydrous sodium sulphate, which when powdered and mixed with water sets like plaster, but being more soluble is more suitable for the experiment. A glass tube, divided midway by means of a piece of metallic gauze, was filled with water, and pieces of fused sodium sulphate were placed on the gauze ; the tube was then plunged into cold water to prevent rise of temperature. After a few hours a solid mass of hydrated sodium sulphate had formed at the bottom of the tube several centimetres away from the anhydrous salt, showing that the setting can take place away from the mass, and is due to the formation of, and crystallisation from, a supersaturated solution.

Investigations on barium cements led to the production of the anhydrous silicates BaSiO_3 and Ba_2SiO_4 by heating together the requisite proportions of silica and barium oxide. The fused mass obtained in the first case, when examined in section under the microscope, appears as an entanglement of long prismatic crystals, with slight double refraction and easy cleavage. The second silicate simply cakes together, and forms a porous mass exhibiting only a confused crystallisation under the microscope. Both these set when mixed with water, owing to the formation of the hydrated silicate $\text{BaSiO}_3 \cdot 6\text{H}_2\text{O}$, which is likewise formed when pulverised calcined silica and barium hydroxide are quenched with water, and when a soluble silicate is added to baryta-water ; in the latter case, it forms a bulky precipitate, which gradually becomes crystalline, and after 24 hours is entirely changed into tabular crystals, identical with those formed in glass bottles containing baryta-water.

The author has made extensive and elaborate investigations on calcareous cements, in the course of which he has made a careful study of the decomposition of calcium carbonate by heat ; all details of the methods and apparatus employed are given in the original. When heated rapidly, decomposition starts from 890° to 930° , according as the carbonate is precipitated carbonate, chalk, or marble ; but if it contains magnesia the decomposition commences at 720° . In more careful experiments it was observed that at the same temperature the tension limit is the same for precipitated carbonate, chalk, or marble, but that the limit is reached with greater rapidity by the precipitate. Below 500° , the decomposition is too slow to admit of accurate experiments ; at 500° , the limit is not reached until after two hours, and then only equals $\frac{1}{10000}$ of the mass experimented on per hour, and a temperature of 812° is required before the tension equals atmospheric pressure.

According to the author's experience, calcium hydroxide, when heated rapidly, decomposes at a temperature of 530° to 540° ; when carefully heated below 100° , there is no appreciable decomposition ; at 350° , the tension of dissociation is only 100 mm. of mercury, and only reaches one atmosphere at 450° . It may, therefore, be considered as quite stable in dry air at ordinary temperatures, and moreover it is only attacked very slowly by carbonic anhydride.

The author has prepared and fully described the anhydrous silicates CaSiO_3 , Ca_2SiO_4 , $\text{Ca}_3\text{Si}_2\text{O}_7$, Ca_3SiO_5 . The first three he prepared by heating together silica and lime in proper proportions; the first is identical with wollastonite, the third is simply a mixture of the first and second. The second forms a hard, solid, fused mass while hot, but as it cools it cracks, swells, and ultimately falls to a white powder, resembling slaked lime; this really consists of microscopic, prismatic, crystalline fragments, slightly doubly refractive, and, at times, striated in the direction of the greatest length. This phenomenon is the result of the dimorphism of this silicate, the change is accompanied by development of heat. The spontaneous pulverisation in some slags and cements is now attributed to the presence of this silicate. This power of pulverisation is diminished by the presence of magnesia, iron oxide, or alumina, hence the pulverisation in slags may be much delayed. With equal molecular proportions of magnesia and lime, the resulting mass remains absolutely compact, hard, and definitely crystallised, it is, in fact, monticellite, CaMgSiO_4 . The compound Ca_3SiO_5 cannot be obtained in the same way as the others by heating lime and silica together, nor by using a flux such as calcium chloride as well, in fact, in the latter case a calcium chlorosilicate is produced. This substance, $\text{Ca}_2\text{SiO}_4 \cdot \text{CaCl}_2$, forms orthorhombic crystals with double cleavage and energetic double refraction; measurements of the crystals are given. The crystals are attacked by water, but not by alcohol. Heated in steam above 450° , it gave rise to an amorphous compound, presumably Ca_3SiO_5 ; neither of the preceding silicates set when mixed with water, but this does, forming a hard, durable briquette, which shows conclusively that it not only differs from them, but that it is also free from uncombined lime. The author could not obtain hydrated silicates by direct hydration of the above anhydrous silicates; the only one prepared by him was $\text{CaSiO}_3 \cdot \text{Aq}$ (possibly $2\frac{1}{2}$ mols. H_2O) by precipitating lime-water with a solution of silica.

The author has also investigated those calcium aluminates which may be expected to occur in cements, and pursuing the synthetical methods by fusion, as adopted in the case of silicates, he has prepared three anhydrous aluminates, and one hydrated aluminate. CaAl_2O_4 , corresponding with spinel, crystallises in scarcely fusible, very hard cubic crystals. $\text{Ca}_3\text{Al}_4\text{O}_9$ (the author is not quite certain about the composition of this salt) forms orthorhombic crystals with very strong double refraction, which fuse with moderate facility. $\text{Ca}_3\text{Al}_2\text{O}_6$ forms easily fusible, cubic crystals. When pulverised and quenched with water, all three set like plaster of Paris, but when agitated with excess of water they decompose, both lime and alumina pass into solution, from which the alumina is partly, or if lime water is added, wholly precipitated in the form of a crystalline hydrated calcium aluminate. This salt, $\text{Ca}_4\text{Al}_2\text{O}_7 \cdot 12\text{H}_2\text{O}$, is the only hydrated calcium aluminate stable in the presence of free lime, and, therefore, capable of existing in wetted cements; it crystallises in spherulitic groups of long needles, forming compact spherulites when the crystallisation is slow. Calcium aluminates become rapidly less susceptible, and ultimately indifferent to the action of water when magnesium is substituted for calcium. The

author does not describe any definite anhydrous calcium ferrate, and only one hydrated ferrate, a white substance decomposed by water and by carbonic anhydride, but not by lime-water. Carbonic anhydride liberates ferric hydroxide.

Mixing alumina and ferric oxide and then heating with lime increases the fusibility of the corresponding lime salts. The author has obtained the aluminoferrate, $\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, 3\text{CaO}$, crystallising in well-defined, long, red needles. By fusing calcium ferrates with calcium chloride, brown plates terminating in symmetrical obtuse points are obtained of the composition $\text{Fe}_2\text{O}_3, \text{CaO}, \text{CaCl}_2$. They have a remarkably easy cleavage, but are not attacked by water or acetic acid. The aluminates under similar circumstances yield very fusible glassy substances, which are decomposed by water.

The rest of this monograph treats of the character and behaviour of the various constituents of cements when they are present in the burnt cementitious mixtures or in the wetted cements. D. A. L.

Action of Alkaline Phosphates on the Alkaline Earths.

By L. OUVRARD (*Compt. rend.*, **106**, 1599—1601).—The oxide or a salt of the alkaline earth was dissolved in the fused phosphate, with or without an alkaline chloride, allowed to cool slowly, and the product treated with water.

Barium oxide dissolves readily in potassium metaphosphate or pyrophosphate, and in both cases yields the pyrophosphate $\text{Ba}_2\text{P}_2\text{O}_7$ in monoclinic prisms which dissolve readily in dilute acids and in concentrated sulphuric acid. In presence of potassium chloride, the result is the same if the proportion of the phosphate is not below 5 per cent., but with a lower proportion a chlorophosphate is formed. Precipitated barium phosphate behaves in the same manner as the oxide. Barium sulphate also dissolves and yields the pyrophosphate, the excess of sulphate crystallising in the form of barytes.

Potassium orthophosphate with barium oxide, chloride, or phosphate, yields the compound $\text{P}_2\text{O}_5, 2\text{BaO}, \text{K}_2\text{O}$ in transparent, dendritic crystals, soluble in dilute acids.

Sodium metaphosphate and pyrophosphate yield either barium pyrophosphate or, if the proportion of barium is considerable, the compound $\text{P}_2\text{O}_5, 3\text{BaO}$, which crystallises in large, transparent lamellæ, seemingly belonging to the regular system; sp. gr. 4.1 at 16°. The crystals dissolve in dilute acids and in concentrated sulphuric acid. Sodium chloride promotes crystallisation, but if the proportion exceeds a certain limit, a chlorophosphate is formed. Sodium orthophosphate yields only the compound $\text{P}_2\text{O}_5, 3\text{BaO}$. Barium sulphate is not decomposed by the sodium phosphates; it dissolves to a certain extent but crystallises unaltered on cooling.

Calcium oxide, phosphate, or sulphate with potassium metaphosphate or pyrophosphate, yield the compound $\text{P}_2\text{O}_5, \text{CaO}, \text{K}_2\text{O}$ in large, transparent hexagonal lamellæ derived from the regular octahedron; sp. gr. 2.7. The same compound is also obtained from calcium chloride or fluoride if the alkaline phosphate is in sufficient excess; it dissolves readily in dilute acids. Tripotassium phosphate and calcium oxide form

the compound $\text{P}_2\text{O}_5, 2\text{CaO}, \text{K}_2\text{O}$, which has the same crystalline form as the corresponding barium salt, and has already been described by Grandeau, who obtained it by Debray's method. Sodium metaposphate yields two products according to the proportion of oxide employed, namely, $9\text{P}_2\text{O}_5, 10\text{CaO}, 8\text{Na}_2\text{O}$, which was previously obtained by Wallroth under the same conditions, and forms monoclinic lamellæ, and $\text{P}_2\text{O}_5, 2\text{CaO}, \text{Na}_2\text{O}$, which has been described by Ditte, and forms transparent hexagonal rosettes. Sodium pyrophosphate and orthophosphate yield the salt $\text{P}_2\text{O}_5, 2\text{CaO}, \text{Na}_2\text{O}$, and also the salt $2\text{P}_2\text{O}_5, 3\text{CaO}, 3\text{Na}_2\text{O}$, which crystallises in slender, transparent, monoclinic needles melting to a white enamel at a red heat. With the carbonate, phosphate, sulphate, chloride, and fluoride, the same products are obtained as with the oxide. With sodium or calcium chloride in excess, chlorophosphates corresponding to apatite and wagnerite are formed.

Strontium oxide and salts with potassium meta- or pyro-phosphate yield the compound $\text{P}_2\text{O}_5, \text{SrO}, \text{K}_2\text{O}$, identical in form with the corresponding calcium salt. Tripotassium phosphate produces the compound $\text{P}_2\text{O}_5, 2\text{SrO}, \text{K}_2\text{O}$, identical in form with the analogous barium and calcium compounds. Sodium meta- and pyro-phosphates yield first the compound $\text{P}_2\text{O}_5, 2\text{SrO}$ in small, rhombic prisms similar to those of the barium salt, and then the compound $\text{P}_2\text{O}_5, 2\text{SrO}, \text{Na}_2\text{O}$ analogous to the product obtained with calcium. Sodium orthophosphate yields only the salt $\text{P}_2\text{O}_5, 2\text{SrO}, \text{Na}_2\text{O}$; strontium sulphate is not decomposed by the sodium phosphates.

Barium is not readily displaced by alkalis and therefore does not readily form double salts. Calcium forms double phosphates only, and strontium occupies an intermediate position. C. H. B.

Decomposition of Barium Ferrate at High Temperatures.

By G. ROUSSEAU and J. BERNHEIM (*Compt. rend.*, **106**, 1726—1728.)—If barium ferrate is introduced into barium chloride or barium bromide fused at $800\text{--}1300^\circ$, it rapidly decomposes with effervescence owing to the liberation of oxygen, and leaves a residue of ferric oxide. If, however, about 3 grams of barium ferrate is added gradually to a fused mixture of 15 grams of barium chloride or bromide, and 5 grams of barium oxide, and the product is treated with water, it yields brownish-black crystals of barium ferrite. At 1100° , about 6 grams of barium oxide is required to prevent the decomposition of the ferrite, and at an orange-red heat 12 grams is necessary. It follows from these results that whereas barium ferrate if heated alone decomposes into oxygen, ferric oxide, and barium oxide, when heated with barium oxide it yields oxygen and barium ferrite. The decomposition of the ferrate in presence of neutral or slightly basic fluxes is analogous to the decomposition of alcoholates by dilution, but the latter is progressive whilst the former takes place suddenly as soon as the proportion of barium oxide has fallen below a certain limit. If barium carbonate is present, it crystallises from the oxychloride which is formed, and the crystals are not readily separated from those of the ferrite. C. H. B.

Double Phosphates in the Magnesium Group. By L. OUVREAU (*Compt. rend.*, 106, 1729—1732.)—These phosphates were obtained in the same way as the phosphates of the barium group (this vol., p. 1033).

Magnesium.—With potassium metaphosphate, the sole product is the compound $3\text{P}_2\text{O}_5, 2\text{MgO}, \text{K}_2\text{O}$, which crystallises in large, monoclinic prisms, very soluble in dilute acids; sp. gr. at $20^\circ = 2.4$. It is analogous to the double magnesium sodium phosphate obtained by Fleitmann and Hennerberg in the wet way.

Potassium pyrophosphate or orthophosphate yields rhombic prisms of the salt $\text{P}_2\text{O}_5, 2\text{MgO}, \text{K}_2\text{O}$, previously described by Grandeau. Magnesium phosphate yields the same products as the oxide, but the chloride yields a chlorophosphate unless the alkaline phosphate is present in considerable excess.

With sodium metaphosphate at a low temperature, the magnesium oxide not being in excess, the salt $9\text{P}_2\text{O}_5, 10\text{MgO}, 8\text{Na}_2\text{O}$ is obtained in highly macled, monoclinic prisms; sp. gr. at $20^\circ = 2.7$. This compound has previously been described by Wallroth. At a high temperature, the metaphosphate yields dendritic crystals of the compound $\text{P}_2\text{O}_5, \text{MgO}, 2\text{Na}_2\text{O}$, and the same product is obtained with the pyrophosphate. It is readily soluble in dilute acids. Sodium orthophosphate yields the salt $2\text{P}_2\text{O}_5, 3\text{MgO}, 3\text{Na}_2\text{O}$ in dendritic crystals which depolarise light.

Zinc and cadmium yield compounds which are strictly analogous. With potassium metaphosphate, the salt $\text{P}_2\text{O}_5, \text{MO}, \text{K}_2\text{O}$ is obtained in highly macled crystals which depolarise light and are soluble in dilute acids. Potassium pyro- or ortho-phosphate yields monoclinic prisms of the salt $\text{P}_2\text{O}_5, 2\text{MO}, \text{K}_2\text{O}$, very soluble in dilute acids. Zinc and cadmium phosphates yield the same products as the oxides, and alkaline chlorides have no effect on the result even when present in large excess. The compound just described can in fact be obtained by the action of cadmium or zinc phosphate on potassium chloride.

Sodium metaphosphate yields the salt $\text{P}_2\text{O}_5, \text{MO}, \text{Na}_2\text{O}$, described by Wallroth, or the salt $\text{P}_2\text{O}_5, 2\text{MO}, \text{Na}_2\text{O}$, described by Scheffer, or a third salt, $\text{P}_2\text{O}_5, \text{MO}, 2\text{Na}_2\text{O}$; according to the relative proportions of the oxides; sodium pyro- or ortho-phosphate yields the compounds $\text{P}_2\text{O}_5, \text{MO}, 2\text{Na}_2\text{O}$ and $\text{P}_2\text{O}_5, 2\text{MO}, \text{Na}_2\text{O}$.

Manganese yields products similar to those obtained with zinc and cadmium, but in presence of an alkaline chloride chlorophosphates are formed if the proportion of alkaline phosphate falls below a certain limit. $\text{P}_2\text{O}_5, \text{MnO}, \text{K}_2\text{O}$ and $\text{P}_2\text{O}_5, 2\text{MnO}, \text{K}_2\text{O}$ crystallise in monoclinic prisms; $\text{P}_2\text{O}_5, \text{MnO}, \text{Na}_2\text{O}$ forms highly macled rose-coloured prisms which are probably triclinic. $\text{P}_2\text{O}_5, \text{MnO}, 2\text{Na}_2\text{O}$ and $\text{P}_2\text{O}_5, 2\text{MnO}, \text{Na}_2\text{O}$ are isomorphous with the corresponding zinc and cadmium salts.

Cobalt and nickel form strictly analogous compounds. Potassium metaphosphate yields monoclinic prisms of the composition



and the pyro- and ortho-phosphate yield rhombic crystals of the salt $\text{P}_2\text{O}_5, 2\text{MO}, \text{K}_2\text{O}$, all soluble in dilute acids. The presence of potassium

chloride promotes crystallisation, but exerts no other influence on the result.

Sodium metaphosphate yields the salt $9\text{P}_2\text{O}_5, 10\text{MO}, 8\text{Na}_2\text{O}$ in macted, dichroic violet or rose-coloured prisms, or, if the oxide is in excess, the salt $\text{P}_2\text{O}_5, 2\text{MO}_3, \text{Na}_2\text{O}$, which is isomorphous with the corresponding zinc salt; sodium pyro- or ortho-phosphate yields products strictly analogous to those obtained with zinc, cadmium, and manganese. In presence of sodium chloride, all the double phosphates of nickel or cobalt are converted into the salt $\text{P}_2\text{O}_5, 2\text{MO}, \text{Na}_2\text{O}$.

C. H. B.

Action of Calcium Carbonate on Cadmium Chloride and Cadmium Bromide. By A. DE SCHULTEN (*Compt. rend.*, **106**, 1674 1677).—When cadmium chloride solution is heated with powdered marble in sealed tubes at 200° , some carbonic anhydride is liberated, but no cadmium carbonate is formed. The liquid, however, deposits small hexagonal crystals which dissolve in hydrochloric acid without effervescence. They have the composition $\text{CdCl}_2, \text{Cd}(\text{OH})_2$, and lose only a small quantity of water at 280° , but become anhydrous at dull redness, the cadmium chloride volatilising to a certain extent. The crystals are hexagonal prisms with transverse striations, terminated by hexagonal pyramids; sp. gr. at $15^\circ = 4.56$. The behaviour of the compound when heated indicates that it has the constitution $\text{Cd}(\text{OH})\text{Cl}$. Similar crystals are obtained by heating cadmium chloride and cadmium hydroxide in sealed tubes; the iodide and bromide likewise attack the hydroxide. Haberman obtained an amorphous precipitate of the same composition by adding dilute ammonia to a boiling concentrated solution of cadmium chloride.

Cadmium bromide yields a similar compound, $\text{Cd}(\text{OH})\text{Br}$, which crystallises in thin, colourless transparent lamellæ; sp. gr. at $15^\circ = 4.87$.

Cadmium iodide and calcium carbonate yield no similar product at 200° .

C. H. B.

Hydrochloride of Cupric Chloride. By P. SABATIER (*Compt. rend.*, **106**, 1724—1726).—When hydrogen chloride is passed into a saturated solution of cupric chloride, heat is developed and the solution becomes brown. If the liquid is cooled, it deposits crystals of the hydrate $\text{CuCl}_2, 2\text{H}_2\text{O}$, and the mother-liquor is greenish-yellow. On exposure to dry air, the crystals become greenish-blue without losing their transparency. The crystals of the ordinary dihydrate remain unaltered in the mother-liquor of the crystals just described, and the latter owe their different appearance to the presence of some of the mother-liquor.

If the quantity of hydrochloric acid in the solution is increased, the solubility of the cupric salt at first decreases, but afterwards increases, as Engel observed in the case of stannous chloride, and the change in solubility corresponds exactly with the point at which the greenish colour of the liquid becomes reddish. If the reddish-brown solution is cooled to 0° , it deposits radiating, acicular, red crystals of the composition $\text{CuCl}_2, 2\text{HCl} + 5\text{H}_2\text{O}$, which rapidly change to crystals of the ordinary hydrate even in concentrated hydrochloric acid, or in a

current of hydrogen chloride. They may, however, be preserved in the mother-liquor at the ordinary temperature. They rapidly lose hydrochloric acid when exposed to air and immediately if placed in water or if heated.

C. H. B.

Hydrochloride of Cupric Chloride. By P. SABATIER (*Compt. rend.*, **107**, 40—41).—The hydrochloride of cupric chloride described by Engel (this vol., p. 558) is probably identical with that described by the author (preceding Abstract), the difference in the analytical results being due to decomposition during the process adopted by Engel for drying the salt.

The author has determined the variations in the solubility of cupric chloride in presence of hydrochloric acid at 21.5°, the result being stated in equivalents of the salt and acid respectively dissolved in 100 equivalents of water.

Hydrochloric acid	0	0.95	1.76	4.19
Cupric chloride	11.91	10.56	8.36	5.69
Sp. gr.....	1.50	1.47	1.44	1.31
Hydrochloric acid..	6.22	7.45	14.02	15.25
Cupric chloride....	4.32	3.86	6.46	7.26
Sp. gr.	1.28	1.27	1.34	1.38
			1.38	1.43

The variations are much greater at 21.5° than at 0°.

C. H. B.

Mercurous Oxide. By W. BRUNS and O. V. D. PFORDTEN (*Ber.*, **21**, 2010—2013).—Mercurous oxide cannot be obtained free from mercury and mercuric oxide. When mercurous acetate is rubbed in a mortar with an excess of alcoholic potash, the product washed with alcohol, then with ether and dried, the mercurous oxide obtained contains metallic mercury even when the whole process is carried out in absence of light, and mercuric oxide is also present in small quantities. Mercurous oxide similarly prepared from aqueous instead of alcoholic solutions, contains the same impurities but in larger quantities.

Mercurous oxide oxidises to mercuric oxide even at the ordinary temperature, and oxidation seems to take place more quickly in presence of moisture. Dry mercurous oxide is completely converted into mercuric oxide and metal when heated at 100° for some time.

F. S. K.

Phosphates of the Cerite Metals. By L. OUVARD (*Compt. rend.*, **107**, 37—40).—When the oxides of cerium, lanthanum, and didymium are fused with alkaline phosphates in the manner previously described (this vol., p. 1033), they yield strictly analogous isomorphous compounds. The cerium and lanthanum oxides were quite pure, and the didymium contained only a very small proportion of other oxides. The formulæ and crystalline forms of the products were as follows:—With potassium metaphosphate the tribasic phosphate, $M_2O_3 \cdot P_2O_5$, in monoclinic prisms; with potassium orthophosphate or pyrophosphate, right rhombic prisms of the salt $3P_2O_5 \cdot 2M_2O_3 \cdot 3K_2O$. The latter is

converted into the tribasic phosphate in presence of potassium chloride; sp. gr. of the cerium salt 3·8; of the lanthanum salt 3·5. Sodium metaphosphate yields monoclinic prisms of the pyrophosphate, $2\text{P}_2\text{O}_5, \text{M}_2\text{O}_3, \text{Na}_2\text{O}$, described by Wallroth, and then, if a larger proportion of the oxide is used, the tribasic phosphates as in the case of the potassium salts. Sodium orthophosphate or pyrophosphate yields the salt $\text{P}_2\text{O}_5, \text{M}_2\text{O}_3, 3\text{Na}_2\text{O}$, which is converted into the tribasic phosphate in presence of sodium chloride.

The simple tribasic phosphates are insoluble in acids, but the double orthophosphates and pyrophosphates are readily soluble.

C. H. B.

Absorption Spectra of Rare Earths. By P. KIESEWETTER and G. KRÜSS (*Ber.*, 21, 2310—2320; compare G. Krüss and L. F. Nilson *Abstr.*, 1887, 890).—Finely divided yttritanite or keilhauite from Arendal was melted in a graphite crucible with flowers of sulphur and soda, the melt well washed with water, and the filtrate treated according to Winkler's method (*Abstr.*, 1886, 985), but no germanium was found. The residue was melted with hydrogen potassium sulphate, extracted with water, the solution acidified with hydrochloric acid, and the bases precipitated as oxalates. The white-grey powder, which remained when the mixture of oxalates was ignited, was dissolved in concentrated nitric acid, the solution freed from nitric acid by repeatedly evaporating, and examined spectroscopically as described (*loc. cit.*) with the following results:—

Observed position of maximum darkness.		Observed wave-length. Krüss and Nilson.	For	Intensity of absorption-bands.
Position of of telescope tympanum.	Observed wave-length.			
421	683·1	684·0	Tm α	Very feeble.
519	654·4	654·7	Er α	Feeble.
863	580·3	579·2	Di γ	Moderately feeble.
895	575·3	575·4	D γ	Feeble, more so than $\lambda = 579\cdot2$.
1106	542·7	542·6	X β	Very feeble.
1128	539·3	539·9	?	Very feeble.
1240	523·0	523·1	Er β	Tolerably strong.
1254	521·3	521·5	Di δ	Strong, stronger than $\lambda = 579\cdot2$.
1589	485·9	485·5	X δ	Moderately feeble, considerably stronger than X β .
2088	452·0	452·6	X ζ	Strong, stronger than X δ .

The Tm α line was identified by a comparison with Tm obtained from Arendal thorite. The line $\lambda = 539\cdot9$ was observed in the spectrum of holmium material, &c., and identified by direct comparison.

The presence of the Di γ and Di δ constituents of didymium, and the absence of other didymium lines is further evidence in support of

the great complexity of didymium. The isolated intensity of the line $X\zeta$ is further evidence that Soret's X-earth is a mixture, and this conclusion is also supported by an examination of the spectra which are given, showing the observed relative intensity of the X lines of keilhauite, brevig-thorite, brevig-wöhlerite, and those of an ordinary holmium material. These spectra show that the constituents of what used to be known as holmium present in thorite, wöhlerite and keilhauite are not identical, and the substance, the nitrate of which gives the line $X\epsilon$ in the holmium spectrum, is not present in keilhauite, brevig-thorite, and brevig-wöhlerite. Traces of uranium were observed in the spectrum of keilhauite from Arendal. It is probable that the substances, the nitrates of which give the lines $Di\delta$ and $X\zeta$, could be easily obtained from this earth.

120 grams of finely divided gadolinite from Hitterö was evaporated several times with concentrated hydrochloric acid, and the filtered solution precipitated with oxalic acid. The yellow oxide obtained by igniting the oxalates was dissolved in nitric acid, and repeatedly evaporated until no free acid was present. The solution was examined spectroscopically with the following results:—

Observed position of maximum darkness.		Observed wave-length. Krüss and Nilson.	For	Intensity of absorption-bands.
Position of telescope tympanum.	Observed wave-length.			
296	727.8	728.3	$Di\alpha$	Moderately strong.
398	690.7	690.5	$Di\kappa$	Very feeble.
419	683.7	684.0	$Tm\alpha$	Feeble.
453	673.5	—	?	Very feeble.
525	653.1	654.7	$Er\alpha$	Moderately feeble, identified by comparison.
574	641.7	640.4	$X\alpha$	Feeble.
733	605.0	—	?	Extremely feeble.
788	592.9	591.5	Di	Very "strong."
863	580.3	579.2	$Di\gamma$	Strong.
895	575.3	575.4	$Di\gamma$	Very strong.
1105	542.8	542.6	$X\beta$	Very feeble.
1128	539.3	539.9	?	Feeble $> \lambda = 539.9$.
1241	522.9	523.1	$Er\beta$	Strong.
1257	520.9	521.5	$Di\delta$	Moderately strong.
1347	511.2	512.2	$Di\epsilon$	Feeble.
1589	485.9	585.5	$X\delta$	Moderately strong.
1728	476.6	477.7	$Sm\beta$	Very feeble.
2084	452.2	452.6	$X\zeta$	Very strong.
2203	444.1	444.7	$Di\iota$	Barely perceptible.
2453	428.2	428.5	$X\eta$	Very feeble.

The qualitative composition of 12 principal fractions, which were obtained from a mixture of the whole of the gadolinite earths, by fractional decomposition of the nitrates, is given in tabular form,

from the results of spectroscopic examination. This table shows clearly that the nitrates of a whole series of elements exist in all the fractions, and the authors conclude that in order to isolate any particular element from gadolinite, euxenite and other similar minerals which are often employed, at least 20—25 kilos. would be required. The desired result can be most easily attained when the choice of material is guided by a spectroscopic examination.

F. S. K.

Vapour-density and Molecular Weight of Aluminium Chloride. By C. FRIEDEL and J. M. CRAFTS (*Compt. rend.*, **106**, 1764—1770).—Nilson and Petterson's experiments on the vapour-density of aluminium chloride (this vol., p. 788) have led them to the conclusion that the molecule of this compound is represented by the formula AlCl_3 , and not by the formula Al_2Cl_6 , as was deduced from the older experiments of Deville and Troost (*Ann. Chim. Phys.* [3], **58**, 257). The authors have previously pointed out that the results obtained by V. Meyer's method are only exact when there is no diffusion of the vapour into the air in the apparatus. At high temperatures, when the volatilisation is very rapid, projection and diffusion must take place to a considerable extent, followed immediately afterwards by condensation in the cool stem of the apparatus. They have therefore redetermined the vapour-density of aluminium chloride by Dumas' method, especial care being taken to obtain the chloride in a perfectly anhydrous condition, and to protect it from moisture during the subsequent operations. The determinations of the vapour-density were preceded by determinations of the vapour-tension.

The aluminium chloride was purified by sublimation, and was obtained in large, colourless crystals, comparatively slightly hygroscopic. Although it volatilises without fusing under ordinary pressure, it melts at 186—187° under a pressure of 2.5 atmos. The results of the determinations of the vapour-tension were as follows:—

Temperature....	167.8°	170.4°	171.9°	175.7°
Vap. tension....	252.1	311.4	316.5	430.7 mm.
Temperature....	182.7°	204.2°	207.5°	213.0°
Vap. tension....	755.4	1793.4	2016.1	2277.5 mm.

The vapour-density was determined at the following temperatures:—218°, 263°, 306°, 357°, 390°, 398°, 400°, 415°, 429°, and 433°. The results obtained agree closely with the value 9.24, calculated from the formula Al_2Cl_6 , and confirm the earlier results of Deville and Troost. The lowest temperature at which Nilson and Petterson made a determination was 440°, and the lower values which they obtained indicate that the vapour-density decreases at a high temperature, a result which may be due to the dissociation of the molecule Al_2Cl_6 into the simpler molecules 2AlCl_3 , analogous to the dissociation of iodine, or decomposition may take place in accordance with the equation $\text{Al}_2\text{Cl}_6 = \text{Al}_2\text{Cl}_4 + \text{Cl}_2$, as in the case of ferric chloride.

The authors' results show that aluminium chloride becomes a perfect gas at 218°, 35° above its boiling point, and the vapour-

density shows no sensible variation between this temperature and 400° . It follows that the molecule of aluminium chloride is correctly represented by the formula Al_2Cl_6 . This conclusion it supported by Louise and de Roux's determinations of the vapour-densities of aluminium methide and aluminium ethide. C. H. B.

Hydrochloride of Cobalt Chloride. By P. SABATIER (*Compt. rend.*, **107**, 42).—In presence of increasing quantities of hydrochloric acid, the solubility of cobalt chloride at first decreases and then increases. The following results were obtained at 19° , and are expressed in equivalents of acid and salt respectively, dissolved in 100 equivalents of water.

Hydrochloric acid..	0	1.99	9.16	12.41	16.24
Cobalt chloride....	7.77	6.13	3.29	4.57	4.70
Sp. gr.....	1.397	1.307	1.256	1.290	1.314

The last solution evolves hydrogen chloride when exposed to the air, and deposits amethyst-coloured needles of the lower hydrate. The variation in solubility leaves little doubt that the solution contains a hydrochloride, and in fact, when cooled it deposits a pale-blue granular crystalline precipitate which, however, decomposes so rapidly that it could not be analysed. C. H. B.

Explosion of a Tube containing Crystals of Chromous Sulphate. By J. M. VAN BEMMELEN (*Rec. Trav. Chim.*, **6**, 202—204).—A closed tube containing dry crystals of chromous sulphate, ($\text{CrSO}_4 + 7\text{H}_2\text{O}$), kept in a cupboard secured from direct light acquired a greenish tint, and suddenly exploded violently, after having been kept for about a year. No odour of sulphurous anhydride was perceptible on opening the cupboard, and the contents of the tube were syrupy. The explosion was possibly caused by the slow evolution of hydrogen in the tube produced by the decomposition of a trace of water by the salt, and the subsequent decomposition of water of crystallisation liberated in the oxidation of the salt.

The chromous sulphate was prepared by reducing chromic chloride, precipitating with sodium acetate, filtering, washing, and drying the product, the whole operation being conducted in an atmosphere of carbonic anhydride. The crystals had a splendid blue colour. A second tube containing more perfectly dried crystals prepared at the same time has not yet exploded, but the crystals are greenish.

N. H. M.

Germanium Oxide. By J. M. VAN BEMMELEN (*Rec. Trav. Chim.*, **6**, 205—208).—Winkler obtained (*Abstr.*, 1886, 985) a gelatinous hydrate of germanium oxide of the formula $\text{GeO} + \frac{1}{2}\text{H}_2\text{O}$ by the action of water on the tetrachloride. The author found the same amount of water in a hydrate of silica obtained under similar conditions (*Arch. Neerland.*, **15**, 330).

When pure germanium oxide is dissolved in water, and evaporated at the ordinary temperature, a hard crust of minute crystals is formed, consisting of the anhydrous oxide; it is not hygroscopic.

Germanium oxide (from the sulphide) when treated with dilute sulphuric acid (1 mol. H_2SO_4 to 4 mols. H_2O) does not dissolve even when heated; the gelatinous oxide, on the other hand, like silicic and stannic acids, retains a certain amount of sulphuric acid.

When a solution of germanium oxide in soda is precipitated with carbonic anhydride, an amorphous substance of an indefinite composition, containing some alkali and water, is formed.

The position of germanium in Mendelejeff and Meyer's tables is in the fourth series between silicium and tin. N. H. M.

Hydrochlorides of Bismuth and Antimony Chlorides. By ENGEL (*Compt. rend.*, **106**, 1797—1800).—The hydrochloride of antimony trichloride is obtained by passing hydrogen chloride into a solution of antimony chloride saturated at 0° until the solution is saturated with the gas, and then cooling it to 0° , when it deposits large crystals of the composition $2\text{SbCl}_3, \text{HCl} + 2\text{H}_2\text{O}$, which melt at 16° with evolution of hydrogen chloride; sp. gr. = 2.388.

The hydrochloride of antimony pentachloride, $\text{SbCl}_5, 5\text{HCl} + 10\text{H}_2\text{O}$, is obtained by adding the pentachloride very gradually to sufficient water to form the hydrate $\text{SbCl}_5, 4\text{H}_2\text{O}$; and when the crystals of the latter begin to separate, hydrogen chloride is passed into the liquid, and water is added until the crystals dissolve. The liquid is then cooled to 0° , when it deposits crystals of the hydrochloride which are stable at the ordinary temperatures. The analytical numbers agree more closely with the formula $\text{SbCl}_5, 5\text{HCl}, 11\text{H}_2\text{O}$, but this is not so probable as the formula given.

The hydrochloride of bismuth chloride, $2\text{BiCl}_3, \text{HCl} + 3\text{H}_2\text{O}$, is obtained by cooling to 0° a saturated solution of bismuth chloride and hydrochloric acid. It forms crystals which are stable at the ordinary temperature.

All these compounds, like all the hydrochlorides hitherto described, contain water of crystallisation. It is noteworthy that in all the hydrochlorides of chlorides now known, the smallest proportion of water present in the crystals is 2 mols. for each molecule of hydrochloric acid. C. H. B.

Reduction of Gold Chloride by Wood Charcoal. By A. GÖRZ (*Zeit. angewand. Chem.*, **1**, 63—65).—The extraction of gold in the wet way promises to supersede the amalgamation process. Plattner's process consists in treating the ore with chlorine gas and then extracting the soluble chlorides with water. The method appears to require further study to adapt it to the conditions of each particular case. Of the various methods for reducing the ore from the solution so obtained, the latest and most satisfactory is that with wood charcoal. Egleston (*Engineering*, **43**, No. 1116) filters the solution slowly through a bed of powdered wood charcoal, 12 parts of which are found necessary for the reduction of one part of gold. The author prefers to mix the charcoal with the solution and stir. He finds that whereas reduction is not complete even after many days in the cold, it is extremely rapid when the solution is heated. From a solution containing 0.106 gram of gold as chloride in 200 c.c., the gold was

completely precipitated by $1\frac{1}{2}$ hour's boiling with 1 gram of charcoal. From some preliminary determinations of the gases evolved during the reduction, the author concludes that the action is a chemical one, the bye-products of which are carbonic acid, hydrogen, oxygen, and hydrogen chloride, but the results are not very conclusive.

M. J. S.

Atomic Weight of Platinum. By K. SEUBERT (*Ber.*, **21**, 2179—2187).—A long reply to Dittmar and M'Arthur (*Trans. of Royal Soc. Edin.*, **33**, 561—633), concluding as follows:—"In studying Dittmar and M'Arthur's paper I have received the impression, which is probably also shared by others, that neither in their method of analysis nor in the manner in which their results are calculated have Dittmar and M'Arthur's results that preference which is claimed over mine, and therefore the first two sentences of their conclusions should be altered as follows:—(1) The value $Pt = 195.0$ ($O = 15.96$), or $Pt = 195.5$ ($O = 16$) obtained by Dittmar and M'Arthur from analyses of potassium platinochloride, is about half a unit too high. (2.) From K. Seubert's experiments, as well as from those of Halberstadt, the mean of 136 analyses gives the value $Pt = 194.5$, or reduced to a vacuum, $Pt = 194.3$; this is, at the present time, the most probable value for the atomic weight of platinum."

F. S. K.

Mineralogical Chemistry.

Rare Copper Minerals from Utah. By W. F. HILLBERAND and H. S. WASHINGTON (*Amer. J. Sci.*, **35**, 298—307).—In ore shipments from the Mammoth mine near Denver, Colorado, several rare copper minerals have been found.

1. *Olivenite*.—This mineral occurs in prismatic tabular crystals for which the following axial ratio was obtained: $a : b : c = 0.93961 : 1 : 0.672606$, a result that differs considerably from that given by Phillips.

2. *Erinite* occurs as a dark green crystalline lining of cavities. Analysis gave the following results:—

CuO.	ZnO.	CaO.	As ₂ O ₅ .	P ₂ O ₅ .	H ₂ O.	Fe ₂ O ₃ .	Total.
57.67	1.06	0.32	33.53	0.10	7.22	0.14	100.04

The sample contained 3.9 per cent. of insoluble matter not included in the analysis. It lost 0.67 per cent. of water over sulphuric acid, a total of 0.78 at 100°, and 1.14 at 280°, leaving 6.08 per cent. firmly combined.

3. *Tyrolite*.—Some doubt exists regarding the identity of this species. It occurs in scaly masses on quartz. It has a bright apple-

green colour, and a hardness of 2·5. Analysis gave the following results:—

CuO.	ZnO.	CaO.	MgO.	As ₂ O ₅ .	P ₂ O ₅ .	H ₂ O.	SO ₃ .	Total.
46·38	trace	6·69	0·04	26·22	trace	17·57	2·27	99·17

4. *Clinoclasite* occurs distinctly crystallised and in globular forms. It is of a dark bluish-green colour, and has a sp. gr. of 4·38 and a hardness of 2·5 to 3. Analysis of material from a globular mass gave the following results:—

CuO.	ZnO.	As ₂ O ₅ .	P ₂ O ₅ .	H ₂ O.	Fe ₂ O ₃ .	SiO ₂ .	Total.
62·44	0·05	29·59	0·05	7·72	0·12	0·06	100·03

5. *Mixite*.—On some specimens of ore was a mineral occurring in delicate tufts of silky needles, which gave on analysis the following results:—

CuO.	ZnO.	CaO.	Bi ₂ O ₃ .	As ₂ O ₅ .	P ₂ O ₅ .	H ₂ O.	SiO ₂ .	Fe ₂ O ₃ .	Total.
43·89	2·70	0·26	11·18	28·79	0·06	11·04	0·42	0·97	99·31

These results agree fairly well with Schrauf's analysis of mixite.

B. H. B.

Production of Phenacite and Emerald. By P. HAUTEFEUILLE and A. PERREY (*Compt. rend.*, 106, 1800—1803).—A mixture of silica 48 parts, beryllia 15 parts, normal lithium vanadate 200 parts, and lithium carbonate 15 parts, was heated in a platinum crucible at 600—700° for 15 days. The product is a mixture of phenacite, quartz, tridymite, and lithium felspar. The presence of lithium compounds facilitates crystallisation, and promotes the formation of lithium felspar, from which the phenacite itself is formed. The phenacite is isolated by treating the product with water and cold dilute hydrofluoric acid. If the mixture has been heated sufficiently long to decompose the whole of the lithium felspar, all the beryllium is converted into phenacite.

Artificial phenacite is obtained in striated rhombohedral crystals, the angle of which varies from 116° 25' to 116° 45', the angle of the natural mineral being 116° 36'. If it has been formed at a high temperature, the dominant form is the prism *d'* terminated by the rhombohedron *p*. It is infusible, and resists even the prolonged action of a hot mixture of concentrated sulphuric and hydrofluoric acids. A trace of vanadium imparts to it a greenish colour.

Emerald is obtained from a mixture of silica 12·506 parts, alumina 3·580 parts, beryllia 2·64 parts, and lithium hydrogen molybdate 2 parts. This mixture is heated at a very low red heat for 24 hours, and the temperature is gradually raised to 800°, at which it is maintained for 15 days. At a higher temperature the emerald is completely converted into phenacite. The crystals of emerald can be separated by simple levigation and the yield with the quantities given is about 15 grams. They have the composition SiO₂ 67·7; Al₂O₃ 19·6; BeO 13·4, which agrees more closely with the calculated numbers than the composition of many natural specimens.

The dominant form is a hexagonal prism *pm*, the height being usually double the diameter of the base; a green colour is given by small quantities of chromic oxide and a yellow colour by ferric oxide. The sp. gr. of some colourless crystals was 2·67. C. H. B.

Nickel Ores from Oregon. By F. W. CLARKE (*Amer. J. Sci.*, **35**, 483—488).—In 1881, extensive deposits of nickel silicates were discovered in Douglas Co., Oregon. The deposits all lie near the surface, in beds from 4 to 30 feet thick. In appearance, the ores are identical with the garnierite and noumeaite of New Caledonia. The silicates vary much in colour and texture, and are unmistakably products of alteration. An analysis of the purest specimen of ore from Riddle, a dark apple-green, compact, and amorphous variety, gave the following results:—

Loss at 110°.	Loss on ignition.	Al ₂ O ₃ + Fe ₂ O ₃ .	SiO ₂ .	MgO.	NiO.	Total.
8·87	6·09	1·18	44·73	10·56	27·57	99·90

Of the country rock surrounding the Oregon beds, a large, clean, fresh specimen was analysed (I), and the olivine (II) separated from it was also analysed, the results being as follows:—

	Ignition.	SiO ₂ .	Al ₂ O ₃ .	Cr ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	NiO.	CaO.	MgO.	Total.
I.	4·41	41·43	0·04	0·76	2·52	6·25	0·10	0·55	43·74	99·80
II.	0·57	42·81	—	0·79	2·61	7·20	0·26	—	45·12	99·36

The rock thus contains nickel, and the olivine separated from it contains even a larger proportion. This fact suggests a probable source of derivation for the nickel in the altered beds of ore, and this view is conclusively proved by the microscopic investigation.

B. H. B.

Diorite Dyke in Orange Co., New York. By J. F. KEMP (*Amer. J. Sci.*, **35**, 331—332).—Recent workings in the Forest of Dean magnetite mine in Orange Co., New York, prove it to be intersected diagonally by a dyke of diorite, some 6 feet in width. The rock is a typical diorite, dark grey in colour, very fine-grained, and having a sp. gr. of 2·925 to 2·974. On analysis it gave the following results:—

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	Loss on ignition.	Total.
48·19	16·79	18·37	6·85	1·32	1·11	5·59	2·31	100·53

The proportion soluble in hydrochloric acid before fusion was 23·5 per cent., of which 18·0 per cent. consisted of ferric oxide. This analysis shows a higher percentage of silica than those of the two dykes described by Hawes from Compton Falls and by Harrington in the neighbourhood of Montreal, also more alumina and iron, but less lime.

B. H. B.

Artificial Production of Micas and Scapolite. By DOELTER (*Compt. rend.*, **107**, 42—43).—Natural or artificial silicates of suitable

composition were heated to dull redness with a small quantity of alkaline fluoride. The proper regulation of the temperature is essential. Amongst the minerals used were hornblende, glaucophane, aluminous augite, garnet, chlorite, and andalusite. The micas obtained were biotite, phlogopite, muscovite, and lepidolite, identical with the natural minerals in crystalline form and optical properties, hardness, sp. gr., &c.

In the preparation of muscovite, scapolite was obtained in quadratic crystals identical in properties with those of the natural mineral.

C. H. B.

New Meteorite from California. By G. P. MERRILL (*Amer. J. Sci.*, 35, 490—491).—This meteorite was found in the San Emigdio Mountains, San Bernardino Co., California. It is of a dull reddish-brown colour, and shows an irregular fracture. It belongs to the chondritic group, and is composed of olivine and enstatite embedded in a base composed of the same minerals in a fragmental and finely divided condition. Nickeliferous iron constitutes 6·21 per cent. of the stone, and occurs in the form of lumps. It is closely associated with pyrrhotite. Very minute colourless crystals of a monoclinic pyroxene also occur. An analysis of the stone gave:—

Metallic portion.	Soluble in HCl.	Insoluble.
6·21	51·26	42·23

The metallic portion yielded—

Iron.	Nickel.	Cobalt.
88·25	11·27	0·48

The soluble portion includes the olivine, iron oxides, and pyrrhotite, whilst the insoluble portion includes the enstatite and pyroxene. The great amount of oxidation which the metallic portion has undergone renders the examination unsatisfactory.

B. H. B.

Organic Chemistry.

Constitution of Paracyanogen and Cyamelide. By E. MULDER (*Rec. Trav. Chem.*, **6**, 199—201).—Klason (Abstr., 1886, 1001), showed that when cyanuric iodide, $N\begin{smallmatrix} \text{CI}\cdot\text{N} \\ \text{CI}\cdot\text{N} \end{smallmatrix} \text{CI}$, is heated, paracyanogen is formed. The constitution of the latter compound may therefore be represented by two closed rings $N\begin{smallmatrix} \text{C}\cdot\text{N} \\ \text{C}\cdot\text{N} \end{smallmatrix} \text{C}$, attached to each other at two of the carbon-atoms.

In view of the formation of isocyanic and cyanuric acids from cyamelide, the constitution $O\begin{smallmatrix} \text{C}(\text{NH})\cdot\text{O} \\ \text{C}(\text{NH})\cdot\text{O} \end{smallmatrix} \text{C}(\text{NH})$ is suggested for

this compound; the formula is also compatible with the readiness with which free isocyaninic acid polymerises to cyamelide.

N. H. M.

Arsenic Cyanide. By G. W. BLYTHE (*Chem. News*, **57**, 245).—When arsenious chloride and mercury cyanide are distilled together, an arsenic cyanide appears to be formed. It is a volatile liquid resembling hydrocyanic acid in appearance and odour, and is decomposed by water, probably yielding arsenious and hydrocyanic acids.

D. A. L.

Titanium Nitrocyanide. By C. REINHARDT (*Zeit. angewand. Chem.*, **1**, 124—126).—A specimen of this substance, obtained from the slag of a blast furnace, was purified by heating with hydrochloric, hydrofluoric, chromic, and sulphuric acids. When ignited in air, it gained 29 per cent. The titanium was determined by fusing with potassium hydrogen sulphate, dissolving in cold water, adding acetic acid and sodium acetate, and boiling: 128.72 per cent. of titanic oxide was obtained. Both these results confirm the formula Ti_5CN_4 . The compound was not volatile even at a white heat.

M. J. S.

Fulminates. By H. W. WARREN (*Chem. News*, **57**, 255—256).—Copper fulminate was obtained by digesting an aqueous solution of silver fulminate with copper turnings. It was then reduced by nascent hydrogen by connecting with a small Daniell's cell. In a few hours all the copper was deposited on the negative platinum electrode, and the solution was found to contain hydrocyanic acid and ammonia in large quantities with some ammonium fulminate. In another experiment, copper ammonium fulminate was obtained by adding excess of ammonia to a solution of copper fulminate. The deep-blue crystals obtained in this manner were dried over sulphuric acid and decomposed with hydrogen sulphide, when copper sulphide, carbamide, and ammonium thiocyanate were obtained. When dry silicon fluoride is passed over silver fulminate moistened with petroleum, silver fluoride is formed and an explosive gas escapes. By the action of chlorine, bromine, or iodine, chloropierin and other allied substances are produced. Experiments on ethyl fulminate are not complete.

D. A. L.

Isolation of the Higher Normal Paraffins from Brown Coal Paraffin. By F. KRAFFT (*Ber.*, **21**, 2256—2265).—350 grams of crystalline "scale-paraffin," obtained from bituminous schale (?) in the neighbourhood of Halle, were submitted to repeated fractional distillation under 15 mm. pressure. The whole distilled at 185—235° in the first operation, but was finally separated into the following normal paraffins; all of which were crystallised from alcohol in order to remove oily impurities.

Heptadecane, $C_{17}H_{36}$ (5 grams), melting at 22° and boiling at 169—170°; sp. gr. 0.7768 at 22.5°.

Octadecane, $C_{18}H_{38}$, in three fractions boiling at 181—182°:

(1) 3.6 grams melting at 26.5—27.5°; sp. gr. 0.7769 at 28°.

(2) 9 grams melting at 27.2—27.6°; sp. gr. 0.7767 at 28°.

(3) 3.9 grams melting at 27.4—27.6°; sp. gr. 0.7766 at 28°.

Nonadecane, $C_{19}H_{40}$, in three fractions boiling at 193° :

- (1) 6.6 grams melting at $31.4-31.8^{\circ}$; sp. gr. 0.7774 at 32° .
- (2) 29.8 grams melting at $31.6-31.9^{\circ}$; sp. gr. 0.7775 at 32° .
- (3) 25.7 grams melting at $31.6-32.2^{\circ}$; sp. gr. 0.7775 at 32° .

Eicosane, $C_{20}H_{42}$, in three fractions boiling at 205° :

- (1) 19.3 grams melting at $35.5-36.5^{\circ}$; sp. gr. 0.7777 at 36.7° .
- (2) 49.4 grams melting at $35.7-36.3^{\circ}$; sp. gr. 0.7777 at 36.7° .
- (3) 4.4 grams melting at $36.3-36.6^{\circ}$; sp. gr. 0.7778 at 36.7° .

Heneicosane, $C_{21}H_{44}$, in three fractions boiling at 215° :

- (1) 8.8 grams melting at $39.8-40.4^{\circ}$; sp. gr. 0.7784 at 40.4° .
- (2) 23.4 grams melting at $39.8-40.2^{\circ}$; sp. gr. 0.7782 at 40.4° .
- (3) 5.8 grams melting at $39.5-40.3^{\circ}$; sp. gr. 0.7784 at 40.4° .

Docosane, $C_{22}H_{46}$, in two fractions boiling at $224-225^{\circ}$:

- (1) 6.2 grams melting at $43.6-44.1^{\circ}$; sp. gr. 0.7781 at 44.4° .
- (2) 10.5 grams melting at $43.6-44.1^{\circ}$; sp. gr. 0.7778 at 44.4° .

Tricosane, $C_{23}H_{48}$ (5.5 grams), boiling at 234° and melting at $47.6-47.8^{\circ}$; sp. gr. 0.7786 at 47.7° .

The total weight of the pure fractions was 263.2 grams.

To prove the identity of these hydrocarbons with the normal paraffins, the various fractions were again rectified or recrystallised from alcohol until their properties were quite constant, and, owing to loss, the total weight of the fractions then only amounted to 216.9 grams.

A second sample of paraffin, sp. gr. 0.7805 at 47.2° , melted at from 42° to 47.2° , distilled between 220° and 270° , and probably consisted chiefly of tricosane and the next two higher homologues, together with decreasing quantities of both higher and lower members of the series.

A third specimen, sp. gr. 0.7804 at 57.5° , melted at 57.5° with previous softening, distilled at $245-295^{\circ}$, and probably contained normal heptacosane ($C_{27}H_{56}$) as chief constituent, somewhat smaller quantities of the two neighbouring homologues, and decreasing quantities of higher and lower members of the series.

All the boiling points given in this paper are for a pressure of 15 mm.

F. S. K.

Preparation of Ethyl Nitrite. By W. R. DUNSTAN and T. S. DYMOND (*Pharm. J. Trans.*, 18, 861-863).—To prepare pure ethyl nitrite the authors dissolve 34.5 grams of pure sodium nitrite in water, make up to 120 c.c., and cool by immersing the vessel in ice and salt. 13.5 c.c. of sulphuric acid is added to a mixture of 32 c.c. ordinary alcohol with an equal volume of water; the liquid is then diluted to 120 c.c., and cooled below 0° . This acid liquid is made to pass gradually through a thistle funnel, with constant stirring, to the bottom of the solution of sodium nitrite in a narrow glass vessel surrounded by ice and salt. At the conclusion of the process a pale-yellow layer of ethyl nitrite is seen floating above the lower layer of sodium sulphate, now semi-solid from the salt crystallising out. The ethyl nitrite thus prepared contains merely traces of alcohol and of water. The former having been removed by agitation with water

in a separating funnel, the latter is eliminated by digestion with anhydrous potassium carbonate.

Thus prepared, the ethyl nitrite is quite pure. It has a sp. gr. of 0.917 to 0.920 at 0° (water at 0° = 1) and boils at 17.5°. It is very unstable in the presence of water, and even of aqueous vapour, especially when acids are also present, although but in minute traces. Hence it can be preserved only when special precautions are taken, as detailed in the paper, and for use in medicine the authors describe the preparation of a 2 per cent. solution in absolute alcohol, with or without addition of glycerol; this solution should be mixed with water only immediately before administration. R. R.

Rhamnose (Isodulcitol). By B. RAYMAN (*Ber.*, **21**, 2046—2052).—When rhamnose is treated with bromine a *bromide* is obtained which is converted by silver carbonate into a *saccharin*, $C_6H_{10}O_5$. This crystallises in concentrically-grouped, slender needles, melts at 140—142°, is readily soluble in water and alcohol, sparingly soluble in ether. The formation of this compound points to the aldehydic nature of the sugar.

When crystallised rhamnose, $C_6H_{12}O_5 + H_2O$, is boiled with amyl alcohol, the compound $C_6H_{11}O_4 \cdot CH(OC_5H_{11}) \cdot OH$ is formed. All alcoholic solutions of rhamnose are lævorotatory: the addition of water destroys this property. (Compare Rayman and Kruis, this vol., p. 667.) N. H. M.

Isodulcitol. By E. FISCHER and J. TAFEL (*Ber.*, **21**, 2173—2176).—Dextrose, galactose, and isodulcitol are only acted on with extreme slowness by sodium amalgam, whereas levulose and mannose are quickly reduced and converted into mannitol. Isodulcitolcarboxylic acid (this vol., p. 806) is converted into normal heptylic acid when 60 grams of the barium salt are heated for 10 hours with 400 grams of hydriodic acid and 25 grams of amorphous phosphorus. F. S. K.

Compounds of Mannitol. By J. MEUNIER (*Compt. rend.*, **106**, 1732—1734).—The author has previously described certain compounds of mannitol with aldehydes (this vol., p. 950). In order to obtain the benzoic compound, the hydrochloric acid solution of mannitol (*loc. cit.*) is mixed with benzaldehyde and agitated for a few minutes, when it deposits the compound $C_6H_5O_3(C_7H_5O)_3$. If boiled with dilute sulphuric acid, it assimilates 3 mols. H_2O and splits up into mannitol and benzaldehyde.

The author proposes to call these compounds *mannitoids*, that just referred to being *tribenzoic mannitoid*. They are not decomposed by dilute sulphuric acid in the cold, but when boiled with sulphuric acid diluted with four times its volume of water they undergo hydrolysis in the way already indicated.

Trivaleric mannitoid is obtained in a similar manner, but the solution must contain less hydrochloric acid and less zinc chloride, and must not have become dark coloured. When cooled to a low temperature, the liquid deposits silky needles which are washed with dilute alcohol. They melt at 91°. Trivaleric mannitoid is not decomposed

by alcoholic potash, but dissolves in sulphuric acid with liberation of valeraldehyde.
C. H. B.

Composition of Iodide of Starch. By F. SEYFERT (*Zeit. angewand. Chem.*, **1**, 15—19).—From the fact that the blue compound, precipitated when starch-paste is mixed with a solution of iodine in potassium iodide (and then hydrochloric acid added), requires as much thiosulphate for decoloration as the same quantity of iodine solution without starch, the author infers that the blue compound contains no iodine in the form of hydriodic acid (comp. Mylius, *Abstr.*, 1887, 568). The amount of starch in a solution can be readily estimated from the amount of iodine it precipitates. An excess of standard iodine solution is added, then some hydrochloric acid. The whole is made up to a known volume, and the precipitate allowed to subside. An aliquot portion of the clear liquid is then titrated. 100 parts of starch precipitate 22.79 of iodine, so that, on the assumption that the precipitate contains nothing else, its formula would be $(C_{24}H_{40}O_{20})_6I_7$.
M. J. S.

Anhydro-bases of Fatty Diamines. By A. W. HOFMANN (*Ber.*, **21**, 2332—2338).—Diacetylenediamine (Mason, *Abstr.*, 1886, 329) is sparingly soluble in ether. It yields a crystalline salt when evaporated at a moderate temperature with hydrochloric acid, but at a higher temperature decomposition sets in. The *platinochloride*, $2C_2H_4(NHAc)_2 \cdot H_2PtCl_6$, forms well-defined, deep-red, rhombic crystals, and is very soluble in water. The *aurochloride*, $C_2H_4(NHAc)_2 \cdot HAuCl_4$, is a yellow, crystalline compound.

Ethyleneethenyldiamine, $C_2H_4 \langle \begin{smallmatrix} N \\ NH \end{smallmatrix} \rangle CMe$, is obtained when diacetyleneamine is distilled or heated above its melting point for a long time, but it is best prepared by heating the diacetyl-derivative in a stream of dry hydrogen chloride. It melts at 88° , boils at 221 — 224° , and is very soluble in water and alcohol, but almost insoluble in ether. The salts are more stable than those of the acetyl-derivative. The *platinochloride*, $(C_4H_8N_2)_2 \cdot H_2PtCl_6$, crystallises in large, pointed prisms, and is very readily soluble in water. The *aurochloride*, $C_4H_8N_2 \cdot HAuCl_4$, crystallises in slender needles, and is far less soluble than the platinochloride.

Ethylenebenzenyldiamine, $C_2H_4 \langle \begin{smallmatrix} N \\ NH \end{smallmatrix} \rangle CPh$, is obtained in like manner from dibenzoyleneethylenediamine. It crystallises from boiling benzene in quadratic prisms, melts at 101° , is very readily soluble in alcohol and ether, less soluble in benzene. The *nitrate*, *hydrochloride*, and *sulphate* are crystalline salts, and readily soluble in alcohol and water. The *platinochloride*, $(C_8H_{10}N_2)_2 \cdot H_2PtCl_6$, crystallises in slender needles, and is sparingly soluble in water. The *aurochloride*, $C_8H_{10}N_2 \cdot HAuCl_4$, crystallises in needles, and is readily soluble in boiling alcohol, but very sparingly soluble in water.

Trimethyleneethenyldiamine, $C_3H_6 \langle \begin{smallmatrix} N \\ NH \end{smallmatrix} \rangle CMe$, prepared in like manner from diacetyltrimethylenediamine, was obtained in the form

of a brown oil. The *platinochloride*, $(C_5H_{10}N_2)_2, H_2PtCl_6$, forms large, rhombic crystals, and is very readily soluble in water. The more sparingly soluble *aurochloride*, $C_5H_{10}N_2, HAuCl_4$, crystallises in needles.

Trimethylenebenzenyldiamine, $C_3H_6 < \overset{N}{\text{NH}} > CPh$, obtained from dibenzoyltrimethylenediamine, is a crystalline compound which melts under water. It is readily soluble in alcohol and ether, more sparingly in benzene, and insoluble in water. The *hydrochloride*, *nitrate*, and *sulphate* are crystalline, and extremely soluble. The *platinochloride*, $(C_{10}H_{12}N_2)_2, H_2PtCl_6$, and *aurochloride* are sparingly soluble.

Propyleneethenyldiamine, $C_3H_6 < \overset{N}{\text{NH}} > CMe$, is obtained from diacetylpropylenediamine as described above. The *platinochloride*, $(C_5H_{10}N_2)_2, H_2PtCl_6$, forms rhombic crystals, and is extremely soluble in water. The *aurochloride*, $C_5H_{10}N_2, HAuCl_4$, crystallises in small needles.

F. S. K.

Hexamethyleneamine-derivatives. By H. E. L. HORTON (*Ber.*, **21**, 1999—2002; compare Legler, *Abstr.*, 1886, 327).—*Hexamethyleneamine tetrabromide*, $C_6H_{12}N_4, Br_4$, is produced when bromine is added to an aqueous solution of hexamethyleneamine, or by the action of bromine-vapour on hexamethyleneamine. It is a red, crystalline compound, and is decomposed when boiled with water.

Hexamethyleneamine dibromide is insoluble in ordinary solvents.

Hexamethylene diiodide, $C_6H_{12}N_4, I_2$, is obtained when an alcoholic solution of the calculated quantity of iodine is added to an aqueous solution of hexamethyleneamine. It is crystalline, and very sparingly soluble in alcohol.

Hexamethylene tetriodide, $C_6H_{12}N_4, I_4$, prepared similarly, crystallises from acetone in brown, microscopic, rhombic plates. It is readily soluble in acetone, chloroform, and carbon bisulphide, and is decomposed when boiled with water.

Chlorine also produces precipitates in solutions of hexamethyleneamine.

F. S. K.

Reaction of Formaldehyde. By J. PLÖCHL (*Ber.*, **21**, 2117—2119).—When a neutral solution of formaldehyde is treated with ammonium chloride or other ammonium salt at the ordinary temperature, the solution becomes strongly acid. On heating the solution, carbonic anhydride is evolved, and trimethylamine is formed. In a similar manner, mono- and di-methylamine are converted into trimethylamine, whilst pure trimethylamine when heated with a formaldehyde solution remains unchanged.

N. H. M.

Action of Hydroxylamine on Acetylacetone. By W. ZEDEL (*Ber.*, **21**, 2178).—The compound obtained by Combes (*Ann. Chim. Phys.*, 1887, 215) by acting on acetylacetone with hydroxylamine is an anhydride of the constitution $< \overset{\text{CH} \cdot CMe}{\underset{CMe \cdot N}{\text{N}}} > O$. It is a colourless oil boiling at 141—142°.

F. S. K.

Homologues of Diacetyl. By H. v. PECHMANN and R. OTTE (*Ber.*, **21**, 2140—2141). The following homologues of diacetyl have been prepared:—Acetylbutyryl boiling at 128°, acetylisobutyryl boiling at 116°, acetylisovaleryl boiling at 137·5°, acetylisocapronyl boiling at 165°, and acetylcrotonyl. All these compounds are, chemically and physically, analogous to diacetyl. No details are given. F. S. K.

Influence of Negative Groups on the Properties of Compounds. By A. P. N. FRANCHIMONT (*Rec. Trav. Chim.*, **6**, 224—234).—Hydrogen-atoms attached to carbon are not attacked by nitric acid at the ordinary temperature when only one carboxyl-group is attached to the same carbon-atom, as is the case of acetic acid; the presence of a second carboxyl-group renders the compound capable of being attacked, as for instance malonic acid. The fact that acetone is readily acted on shows that it is the carboxyl-group which has the effect of making compounds unable to resist the action of nitric acid, whilst this effect is diminished by the presence of an OH-group attached to carbonyl, but not by methyl. Glycocine, propionic, isobutyric, and succinic acids do not react with nitric acid at the ordinary temperatures, whilst levulinic acid does, owing to the presence of a second carboxyl-group. Hydrogen in ammonia, methylamine, &c., is not attacked by nitric acid, except when a carboxyl-group is attached to the nitrogen; on the other hand, the union of a second carboxyl-group with the nitrogen seems to diminish its effect, diacetamide being less readily attacked than acetamide. Succinimide in which the NH-group forms a chain with the carbon-atoms, does not react with nitric acid. Ethylenecarbamide is also not decomposed by nitric acid. The influence of imidogen seems to be less than that of carboxyl, whilst the simultaneous presence of both groups seems to diminish the effect of the latter, and increase that of the former. In benzene, the six CH-groups so influence each other as to make some of them capable of reacting with nitric acid; the introduction of NO₂ or other negative groups has the effect of making the further action of nitric acid more difficult. The same is observed with nitroethane, which does not yield a dinitro-compound at the ordinary temperature. (Compare Ostwald, *Lehrbuch d. allgem. Chem.*) N. H. M.

Action of Sodium on Ethyl Chloracetate. By R. FITTIG and A. ERLÉNBACH (*Ber.*, **21**, 2138—2140).—An ethyl salt, C₈H₁₃ClO₄, is formed when ethyl chloracetate is gradually added to sodium covered with ether, and the resulting sodium-derivative decomposed with dilute hydrochloric acid. It boils at 157° (45 mm. pressure), cannot be distilled under the ordinary pressure, and is insoluble in water. It yields a *sodium*-derivative, C₈H₁₂ClO₄Na, and a *copper*-compound which crystallises from light petroleum in slender, green needles.

A compound, C₈H₁₄O₄, is obtained, when the preceding substance is reduced with zinc and acetic acid, in the form of a colourless liquid which boils at 106° (14 mm. pressure), and is rather soluble in water. It yields a *sodium*-derivative, C₈H₁₃O₄Na, and a crystalline copper compound, (C₈H₃O₄)₂Cu, which melts at 138°, is readily soluble in

ether, chloroform, and benzene, and when treated with aluminium acetate is converted into a crystalline *aluminium*-compound.

Acetoisopropyl alcohol, $\text{COMe}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, is formed, together with ethyl alcohol and carbonic anhydride, when the preceding compound is boiled with dilute hydrochloric acid. It is a colourless, mobile liquid, boils at 128° , and is miscible with water in all proportions, but is separated from the solution by potassium carbonate. It combines with hydrogen sodium sulphite, forming a crystalline, readily soluble compound, yields a yellowish liquid hydrazide, and combines with hydroxylamine.

When the compound $\text{C}_8\text{H}_{13}\text{ClO}_4$ is left for some time in contact with cold water, it decomposes into alcohol, hydrochloric acid, and a compound, $\text{C}_{12}\text{H}_{14}\text{O}_7$, which is sparingly soluble in water, and crystallises in long, yellow needles melting at $139\cdot5^\circ$. The smallest quantity of this substance colours water deep bluish-violet, which changes to yellow when the solution is boiled. It gives an amorphous *barium* salt, $\text{C}_{12}\text{H}_{12}\text{O}_7\text{Ba}$, and a crystalline *calcium* salt, $\text{C}_{12}\text{H}_{12}\text{O}_7\text{Ca}$, both of which are insoluble in water.

F. S. K.

Formation and Decomposition of Ethereal Salts: Action of Acids on Tertiary Amyl Acetate. By D. KONOWALOFF (*Zeit. physikal. Chem.*, 2, 6—12).—The action of the haloid derivatives of acetic acid has been studied. Trichloroacetic acid acts rapidly at 99° , but the action becomes less rapid as the temperature decreases, and at 50° is 50 times slower than at 99° . At the higher temperature, 75 per cent. of the acetate is decomposed in six hours, some being converted into trichloroacetate. Dichloroacetic acid at 99° decomposes 77 per cent. of the acetate in 24 hours, with the formation of some dichloroacetate. Monochloroacetic acid requires a temperature of 156° to effect an appreciable decomposition, 87 per cent. being then decomposed in two hours. The intention was to have calculated the constants of velocity of these reactions, but owing to the action of the acetic acid set free there is an acceleration as the action proceeds, which interferes with its regular course. The amount of decomposition during the first hour in which this acceleration is at a minimum, if compared with the numbers given by Ostwald for the coefficients of velocity of the above acids, shows, however, that these experiments would give coefficients of velocity of the same order.

H. C.

Preparation of Normal Valeric Acid and Dipropylacetic Acid from Ethyl Malonate. By E. FÜRTH (*Monatsh.*, 9, 308—322; compare Sedlitzky, this vol., p. 250).—To prepare normal valeric acid the author heats zinc with commercial ethyl malonate and normal propyl iodide in a water-bath for 8—10 hours. The nearly solid products of reaction are repeatedly treated with hydrochloric acid and water, and the ethyl propylmalonic acid dried, fractionated, and converted into barium salt, from which propylmalonic acid is obtained pure by shaking it with hydrochloric acid and ether, allowing the ethereal solution to evaporate, and repeatedly crystallising from benzene. The propylmalonic acid is converted into normal valeric

acid by heating it at 180° in a flask provided with an inverted condenser. The pure acid thus formed boils at $186-186.4^{\circ}$.

Silver normal valerate is best prepared by heating diluted valeric acid with excess of silver oxide. On cooling, the solution deposits the salt in the form of wool-like masses of needles, the solubility coefficient of which is—

$$L = 0.2294 + 0.002668(t - 0.3) + 0.00004543(t - 0.3)^2.$$

Calcium normal valerate crystallises in scales. Its solubility coefficient is—

$$L = 10.238 - 0.07643(t - 0.3) + 0.0006293(t - 0.3)^2.$$

whilst that of the barium salt is given by the formula—

$$L = 21.658 - 0.12348(t - 0.3) + 0.001767(t - 0.3)^2.$$

Dipropylmalonic acid is obtained as a bye-product in the preparation of normal valeric acid as above described. On heating at $180-200^{\circ}$ it yields a dipropylacetic acid, identical with that described by Burton (*Abstr.*, 1882, 509). It furnishes a silver salt only slightly soluble in water, an uncrystallisable barium salt, and a calcium salt crystallising in masses of interlaced needles containing 2 mols. H_2O , and having the coefficient of solubility—

$$L = 9.530 - 0.12516(t - 0.3) + 0.0003358(t - 0.3)^2.$$

G. T. M.

Constitution of Ethyl Sodacetoacetate. By A. MICHAEL (*J. pr. Chem.* [2], 37, 473—530; compare this vol., 674).—Ethyl carbethoxacetoacetate was prepared by the action of ethyl chlorocarbonate on ethyl sodacetoacetate in alcoholic solution, also on the dry salt in dry ether, and on the sodium salt obtained by the action of sodium on a weak ethereal solution of ethyl acetoacetate; in all cases the product is identical, boiling at 127° unchanged (at 17 mm. pressure); it is insoluble in concentrated sodium hydroxide, but is decomposed by a weak solution, after remaining in the cold, into carbonic anhydride and alcohol; it is decomposed by alcoholic sodium ethoxide with formation of carbonic anhydride; by careful treatment in the cold with dry sodium ethoxide, ethyl acetoacetate is formed, but no sodium-derivative of the original salt can be obtained.

Ethyl acetomalonate was prepared, after Lange, by acting on an ethereal solution of ethyl sodiomalonate with acetic chloride; the product was fractionated at 17 mm. pressure, and gave ethyl acetomalonate, boiling at 120° , and ethyl diacetomalonate, boiling at 156° . The latter decomposes when heated at the ordinary pressure, and is a neutral oil dissolving slowly in alkalis, with separation of carbonic anhydride. The former is not completely separable from the latter by its lower boiling point, but can be dissolved by weak alkalis, and precipitated from the solution by mineral acids; its sodium-derivative, $C_6H_3NaO_3$, is easily obtained by the action of alcoholic sodium ethoxide as white prismatic leaves, sparingly soluble in alcohol, insoluble in ether, and freely soluble in water.

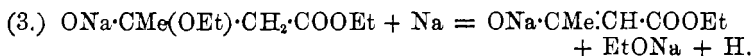
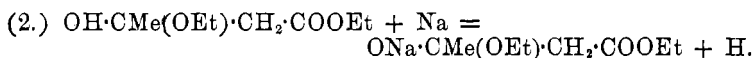
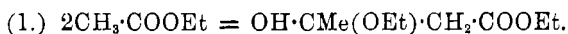
The presence of carbonyl in the ether is shown by its behaviour

with hydroxylamine, with which it forms a half-fluid oxime, and phenylhydrazine with which it forms, at 119—121°, white prismatic leaves of the azide, $\text{CH}_3\cdot\text{CN}_2\cdot\text{HPh}\cdot\text{CH}(\text{COOEt})_2$.

Ethyl methenyltricarboxylate was obtained after Conrad and Guthzeit (Abstr., 1883, 45) by acting on ethyl sodiomalonate in the cold with ethyl chlorocarbonate. The product was fractionated at 17 mm. pressure, and an oil boiling undecomposed at 137—138° obtained, which solidified on standing, and melted at 28—29°. This substance agrees in physical properties with that obtained by Conrad and Guthzeit, but it differs from it in chemical properties. It dissolves readily in weak alkaline solutions, forming metallic derivatives, and is precipitated unchanged from the solution by mineral acids. If heated with excess of potassium hydroxide, malonic acid, alcohol, and potassium carbonate are formed. With concentrated soda solution, the sodium salt, $\text{C}_{10}\text{H}_{15}\text{NaO}_6$, is obtained in white crystals, soluble in water.

In the author's opinion the only two arguments of any weight against ethyl acetoacetate being a ketone-derivative, are that ethyl bezalacetoacetate does not behave as a ketone, and that several ethyl ketonates resembling ethyl acetoacetate yield true acetyl-derivatives, whereas one cannot be formed from ethyl acetoacetate. He explains away the first objection by supposing that a polymerisation of the benzaldehyde and ethyl acetoacetate first takes place, and that the substance formed then loses water, the ketone character of the ethyl bezalacetoacetate being lost. To meet the second objection the author adduces the formation of acetyl-derivatives from ethyl succinosuccinate, levulinate, and acetophenonecarboxylate; these compounds are undoubtedly ketones, for they all give reactions for carbonyl.

The author supposes that in the formation of ethyl sodacetoacetate from sodium and ethylacetate, an "aldol" polymerisation first takes place, and the sodium acts on the substance so formed.

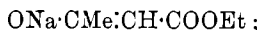


This would make ethyl sodacetoacetate a derivative of ethyl β -hydroxycrotonate, which has been already suggested by Geuther.

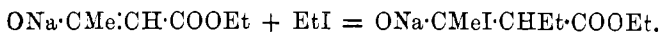
The carbon in methane will be made more negative by the substitution of a negative radicle for one of the hydrogen-atoms, and the attraction between the negative carbon and positive hydrogen will be weaker than in methane. In the same way the ketone oxygen in ethyl acetoacetate is more negative than in acetone, since the ethyl acetoacetate is formed from acetone by displacing positive hydrogen by the negative carbethoxyl.

Ethyl sodacetoacetate when first formed is $\text{COMe}\cdot\text{CHNa}\cdot\text{COOEt}$,

but owing to the strongly negative character of the carbonyl oxygen the sodium is attracted to it, and the formula becomes



in this the β -carbon-atom is less negative than the α -carbon-atom, being influenced by the positive sodoxyl and methyl. Thus when an alkyl haloid, for example, ethyl iodide, acts on ethyl sodacetoacetate, the negative iodine unites with the less negative β -carbon-atom, whilst the ethyl unites with the α -carbon-atom—



But this is unstable, owing to the attraction of the sodium for the iodine, and consequently decomposes into sodium iodide and



By consideration of the influence of positive and negative radicles on the original condition of the compounds, the author explains various reactions of ethyl sodacetoacetate and its analogues. The rest of the paper consists of applications of this theory to various other classes of organic compounds.

A. G. B.

Ethyl Glycidate. By P. MELIKOFF and N. ZELINSKY (*Ber.*, **21**, 2052—2055).—*Ethyl glycidate*, $\langle \overset{\text{O}}{\text{CH}_2} \rangle \text{CH}\cdot\text{COOEt}$, is prepared by gradually adding ethyl iodide to silver glycidate previously mixed with absolute ether, and heating the mixture for some hours on a water-bath. It is a colourless, mobile liquid, of an odour something like that of ethyl malonate, and boils at 161—163° (uncorr.). Sp. gr. = 1.0968 at 21.6°, compared with water at 21.6°, and 1.0933 compared with water at 4°.

Ethyl α -methylglycidate, $\langle \overset{\text{O}}{\text{CH}_2} \rangle \text{CMe}\cdot\text{COOEt}$, is liquid, is insoluble in water, and boils at 162—164°. Sp. gr. = 1.0545 at 15°, and 1.0686 at 0°. Coefficient of expansion = 0.000855.

Ethyl β -methylglycidate, $\langle \overset{\text{O}}{\text{CHMe}} \rangle \text{CH}\cdot\text{COOEt}$, is a liquid of an unpleasant odour, and boils at 172—174°. Sp. gr. = 1.0534 at 15°, and 1.0658 at 0°. The coefficient of expansion = 0.030785.

Ethyl α - β -dimethylglycidate, $\langle \overset{\text{O}}{\text{CHMe}} \rangle \text{CMe}\cdot\text{COOEt}$, boils at 177—178° under 760 mm. pressure. Sp. gr. = 1.0250 at 15°, and 1.0377 at 0°. The coefficient of expansion = 0.000827.

All the above ethyl salts are readily hydrolysed by potash. The alcoholic solutions give no colour reactions with ferric chloride.

Ethyl β -glyceric acid, $\text{OH}\cdot\text{CHMe}\cdot\text{CH}(\text{OH})\cdot\text{COOEt}$, boils at 225—230°, and is readily soluble in water.

N. H. M.

Action of Ethyl Sodiomalonate on Monochloromethyl Ether. By C. KLEBER (*Annalen*, **246**, 97—114).—As the preparation of monochloromethyl ether by the exposure of chlorine and methyl ether vapour to diffused sunlight is accompanied by violent explosions, the

author diluted the chlorine with an equal volume of carbonic anhydride. In this way, about 40 grams of the crude product were formed. This was saturated with dimethyl ether, and a continuous current of dimethyl ether vapour and chlorine was passed into the mixture. This method gave a good yield of monochloromethyl ether.

The chief products of the action of ethyl sodiomalonate on monochloromethyl ether are *ethyl methenedimalonate* and *diethyl dimethoxydimethylmalonate*. These substances are separated by adding a solution of sodium in absolute alcohol to the crude product, which causes the sodium compound of ethyl methenedimalonate to be deposited in a crystalline mass. Methenedimalonic acid has already been described by Conrad and Guthzeit as "dicarboxyglutaric acid" (*Annalen*, **222**, 257).

Dimethoxydimethylmalonic acid, $C(CH_2\cdot OMe)_2(COOH)_2$, forms triclinic prisms, and is freely soluble in water, alcohol, and ether. The diethylic salt is a colourless oil, boiling between 235° and 243° . The free acid melts at 136 — 138° when rapidly heated, but if the temperature is slowly raised it gives off carbonic anhydride at 120° , and at a higher temperature methyl alcohol and methoxymethacrylic acid.

W. C. W.

Symmetrical Diethylsuccinic Acids. By C. A. BISCHOFF and E. HJELT (*Ber.*, **21**, 2089—2097, 2097—2102, and 2102—2111).—*Ethyl ethylbutenyltricarboxylate* is obtained by the action of ethyl α -bromobutyrate on ethyl sodioethylmalonate, and by the action of ethyl iodide and sodium ethoxide on ethyl butenyltricarboxylate. It boils at 280 — 282° . Sp. gr. = $1\cdot024$ at $22\cdot5^\circ$ (water at $15^\circ = 1$). The free acid, $C_9H_{14}O_6$, melts at 150° with evolution of carbonic anhydride and formation of two isomeric diethylsuccinic acids: parasymmetrical diethylsuccinic acid, which is sparingly soluble and melts at 189 — 190° , and antisymmetrical diethylsuccinic acid which is readily soluble and melts at 129° .

Ethyl butenyltricarboxylate boils at 276° under $754\cdot7$ mm. pressure without decomposition; sp. gr. = $1\cdot049$ at $25\cdot5^\circ$ (water at $15^\circ = 1$). (Compare Polko, this vol., p. 134.)

Parasymmetrical diethylsuccinic acid (m. p. 189°) crystallises in monoclinic plates. 100 c.c. of water at 23° dissolve $0\cdot61$ gram of the acid, whilst 100 parts of water at 95° dissolve $6\cdot7$ grams. The acid is readily soluble in acetone, alcohol, ether, and hot glacial acetic acid. The sodium salt, $C_8H_{12}O_4Na_2$, is amorphous and dissolves readily in water; the calcium with 2 mols. H_2O , copper with 1 mol. H_2O , silver and zinc with 2 mols. H_2O , are also described.

Antisymmetrical diethylsuccinic acid forms rhombic crystals. 100 c.c. of water at 23° dissolve $2\cdot4$ grams of the acid which is very soluble in boiling water, in glacial acetic acid, acetone, ether, and alcohol. When quickly heated, it is converted into the anhydride boiling at 245 — 246° . The calcium salt with 1 mol. H_2O is a pulverulent precipitate, the sodium, copper with 1 mol. H_2O , and zinc (with 6 mols. H_2O) salts are described. Both acids when heated with resorcinol form fluorescein dyes.

Parasymmetrical diethylsuccinic acid undergoes no change when boiled with water for 32 hours. When $4\cdot5$ grams of the acid is

heated for two hours at 196° , and the temperature gradually raised during two hours to 218° , 0.14 gram of the anti-acid and 3.8 grams of anhydride are formed. The anti-acid may be reconverted into the para-acid by heating 5 grams of it with 20 c.c. of hydrochloric acid (sp. gr. = 1.1452), or by heating it with water at 190° for 18 hours.

The isomerism of the symmetrical diethylsuccinic acid, which follows that of tartaric and anti-tartaric acids and Reimer's two dibenzylidicarboxylic acids, is discussed. N. H. M.

Determination of the Arrangement of Atoms in Space.

Part I. Fumaric and Maleic Acids. By J. WISLIZENUS (*Annalen*, **246**, 53—96).—The author has pointed out in his treatise "Ueber die räumliche Anordnung der Atome in organischen Moleculen" the existence of two facts which are opposed to the author's theory of the constitution of fumaric and maleic acids, namely, (1) Petri's statement (Abstr., 1879, 373) that fumaric acid is the sole product of the action of bromine on maleic acid in the presence of water, at the ordinary temperature; and (2) the formation of dibromosuccinic acid by the addition of bromine to acetylenedicarboxylic acid as described by Bandrowski (Abstr., 1880, 160).

The action of bromine and water on maleic acid is more complicated than Petri believed. Isodibromosuccinic acid is formed in the first instance, and this acid decomposes, yielding hydrogen bromide and bromofumaric acid. The hydrogen bromide unites with maleic acid, forming monobromosuccinic acid, which afterwards splits up into fumaric and hydrobromic acids.

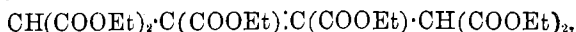
The chief products of the action of bromine on acetylenedicarboxylic acid in the presence of a small quantity of water are dibromofumaric, monofumaric, and hydrobromic acids. Carbonic and oxalic acids are also formed as well as small quantities of mono- and di-bromomaleic acids. By increasing the proportion of water the yield of dibromomaleic acid is increased, because the action of the hydrobromic acid produced in the primary reaction is weakened by dilution. The proportion of maleic to fumaric acid increases with the temperature at which the maleic acid is decomposed. The temperature must not, however, exceed 230° . W. C. W.

Unsaturated Acids. By G. PUM (*Monatsh.*, **9**, 446—457).—*Ethyl bromomaleate* or *bromofumarate* is formed when ethyl dibromosuccinate (1 mol.) is treated with sodic ethoxide (1 mol.) in alcoholic solution; it is a colourless liquid boiling at 145 — 155° (30 mm. pressure).

Ethyl acetylenedicarboxylate is obtained when ethyl dibromosuccinate (1 mol.) is treated with an alcoholic solution of sodic ethoxide (2 mols.).

Ethyl dibromomaleate, prepared by brominating the preceding compound, is a colourless, oily liquid boiling at 170 — 175° (15 mm. pressure) with slight decomposition.

Methyl dibromomaleate is a colourless, oily liquid boiling at 158° (20 mm. pressure).

Hexethyl dimalonylmaleate,

is obtained by treating ethyl dibromomaleate with ethyl sodiomalonate in alcoholic solution. It crystallises in long needles, melts at 75° , boils at $210\text{--}212^\circ$ (15 mm. pressure), and is readily soluble in absolute alcohol, ether, and chloroform, but only sparingly soluble in cold, dilute alcohol.

Dimalonylmaleic acid, $\text{C}_{10}\text{H}_8\text{O}_{12}$, crystallises in small plates, begins to melt at 148° with evolution of carbonic anhydride, and is very readily soluble in water, alcohol, and ether.

The *sodium salt*, $\text{C}_{10}\text{H}_7\text{O}_{12}\text{Na}_6 + 10\text{H}_2\text{O}$, is moderately soluble in water, and crystallises in thick, quadratic plates which lose their water when kept over sulphuric acid or when dried at 120° . The *silver salt*, $\text{C}_{10}\text{H}_7\text{O}_{12}\text{Ag}_6$, is crystalline and explodes when heated. Lead acetate, baric chloride, calcic chloride, and copper sulphate produce precipitates in a warm, neutral, aqueous solution of the ammonium salt.

Hexamethyl dimalonylmaleate, $\text{C}_{10}\text{H}_{20}\text{O}_{12}\text{Me}_6$, prepared from methyl dibromomaleate and methyl sodiomalonate, crystallises from alcohol in shining, white needles, melting at $128\text{--}130^\circ$.

Diglycolylmaleic acid, $\text{C}_2(\text{COOH})_2(\text{CH}_2\cdot\text{COOH})_2$, is obtained when dimalonylmaleic acid is heated at about $150\text{--}160^\circ$ or evaporated with hydrochloric acid. It crystallises from water in colourless, prismatic forms, melts at 176° , and is readily soluble in ether, alcohol, and water.

F. S. K.

Molecular Weight of Citraconic, Itaconic, and Mesaconic Acids, also of Fumaric and Maleic Acids. By E. PATERNO and R. NASINI (*Ber.*, **21**, 2156—2158).—From determinations of the molecular weights of citraconic, itaconic, and mesaconic acids by Raoult's method, the authors conclude that these acids are not polymeric, but isomeric, compounds. The results obtained with itaconic and mesaconic acids are in accordance with the molecular formula $\text{C}_5\text{H}_6\text{O}_4$. In dilute solutions of citraconic acid, the depression deviates very considerably from the normal value, probably owing to decomposition of the molecule into anhydride and water, but in concentrated solutions the depression is normal for the molecular formula $\text{C}_5\text{H}_6\text{O}_4$.

Experiments with maleic and fumaric acids show that they are isomeric. The abnormally high results obtained with the latter indicating decomposition into anhydride and water.

In aqueous solutions of dulcitol the values obtained agree with the molecular formula $\text{C}_6\text{H}_{14}\text{O}_6$, it is therefore isomeric with mannitol. Sorbin has the molecular formula $\text{C}_6\text{H}_{12}\text{O}_6$, and is isomeric with glucose.

F. S. K.

Formation of Saccharic Acid as a Test for Dextrose in Raffinose and other Carbohydrates: Formation of Furfuraldehyde as a Test for Arabinose. By R. GANS, W. E. STONE, and B. TOLLENS (*Ber.*, **21**, 2148—2152).—Dextrose, or any carbohydrate from which dextrose can be obtained, yields saccharic acid when

5 grams of the substance is treated with a suitable proportion (generally 1:6) of nitric acid, sp. gr. 1.15 (compare this vol., p. 820). This reaction can be conveniently employed for the detection of dextrose, as the saccharic acid is easily identified by analysing the silver salt. Lævulose, galactose, sorbose, and arabinose do not yield saccharic acid by this treatment, but from 5 grams of raffinose silver saccharate can be obtained, and larger quantities (200 grams) yield a crystalline acid which is very similar to, and perhaps identical with, saccharolactone acid. Milk-sugar gives the same acid.

Salap mucus gives saccharic acid and therefore also contains dextrose. Quince mucus contains arabinose but no dextrose.

Pure arabinose does not yield lævulinic acid when treated with sulphuric or hydrochloric acid, but when 5 grams of arabinose are distilled with sulphuric acid of a certain concentration a considerable quantity of furfuraldehyde is obtained, the quantity of which can be estimated by concentrating the distillate, adding ammonia, and weighing the furfuramide produced. Gum arabic, cherry gum, traganth, &c., and other compounds containing arabinose behave similarly. Arabinose yields about 20 per cent., the gums, &c., from 5 to 9 per cent. of furfuramide; 5 grams of dextrose, cane-sugar, galactose, sorbose, and other carbohydrates yield only inappreciable quantities of furfuraldehyde, and the distillate gives a very much less marked reaction with aniline acetate than the distillate obtained from arabinose, &c. Koch's wood-sugar or xylose yields a large amount of furfuraldehyde, but Carrageen moss gives only inappreciable quantities.

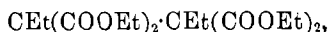
Crystalline carbohydrates can be obtained from wheat bran and more especially from the undissolved portions of malt remaining in the manufacture of beer. These carbohydrates, one of which crystallises in needles and has the specific rotatory power $[\alpha]_D = 103^\circ$, are very nearly related to arabinose.

F. S. K.

Action of Dilute Mineral Acids on Saccharic Acid. By H. SCHRÖTTER (*Monatsh.*, 9, 442—445).—The author has obtained results similar to those published by Sohst and Tollens (this vol., p. 820), and for the preparation of large quantities of dehydromucic acid employed the following method:—Potassium saccharate is boiled with double its weight of 30 per cent. hydrochloric acid for about three days, the filtered solution mixed with one-third its weight of concentrated hydrochloric acid and again boiled for three days; this operation is repeated as long as any separation takes place, and is generally finished in about nine days. The yield is 16 to 18 per cent. of the acid employed. Only one barium salt was obtained; it crystallised with $3\frac{1}{2}$ mols. H_2O , and lost all its water at 115° . Only one acid was obtained by reducing dehydromucic acid with sodium amalgam; it crystallises in white, anhydrous needles, melts at 148 — 149° , and its barium salt crystallises with $4\frac{1}{2}$ mols. H_2O . Dehydromucic acid does not react either with acetic oxide or with hydroxylamine.

F. S. K.

Ethyl Acetylenetetra-carboxylate. By C. A. BISCHOFF (*Ber.*, 21, 2085—2089).—Ethyl diethylacetylenetetra-carboxylate,



is obtained by mixing 110 grams of ethyl ethylmalonate with a solution of sodium ethoxide (from 13.4 grams of sodium) and boiling the mixture with 130 grams of ethyl chlorethylmalonate for 40 hours. It is a colourless oil, insoluble in water, and boils at 198—200° under 11.8—4 mm. pressure; sp. gr. = 1.043 at 19° (water at 15° = 1). The salt is not readily saponified by aqueous hydrochloric acid, the reaction being incomplete after eight days' boiling; when the resulting oil is dissolved in cold concentrated sulphuric acid and water added drop by drop, diethylsuccinic acid, melting at 188°, is formed.

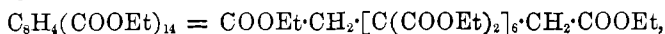
When a mixture of 7.5 grams of sodium, 80 grams of alcohol, 52.2 grams of ethyl malonate, and 72.5 grams of ethyl chlorethylmalonate is boiled for 58 hours, the ethyl salts of acetylenetetra-carboxylic acid and its diethyl-derivative are formed. N. H. M.

Ethyl Dicarboxyglutarate. By M. GUTHZEIT and O. DRESSEL (*Ber.*, 21, 2233—2235).—Ethyl dicarboxyglutarate (comp. Abstr., 1883, 311) can be easily prepared in large quantity by treating ethyl sodiomalonate with methylene iodide in alcoholic solution. The yield of the pure salt is 70 to 80 per cent. It is a tolerably thick, transparent oil boiling at 200—203°, and is identical with ethyl propane-tetra-carboxylate (Perkin, Abstr., 1886, 691) and with ethyl methylenedimalonate (Kleber, this vol., p. 97). The free acid melts at 168—170° with evolution of carbonic anhydride and formation of glutaric acid. F. S. K.

Synthesis of Polybasic Fatty Acids. By C. A. BISCHOFF (*Ber.*, 21, 2111—2117).—Ethyl propionylpentacarboxylate has a sp. gr. = 1.121 at 15°. The *potassium* and *barium* salts (each with 4 mols. H₂O) were prepared. The *free acid* crystallises from ether in globular groups, and melts at 149—151° with evolution of carbonic anhydride. When the ethyl salt is treated with dry chlorine at 70°, the compound $\text{COOEt}\cdot\text{CH}_2\cdot\text{C}(\text{COOEt})_2\cdot\text{CCl}(\text{COOEt})_2$ is formed. When this is treated in the usual manner with ethyl sodiopropionylpentacarboxylate, *ethyl hexaïndecacarboxylate*, $\text{C}_8\text{H}_4(\text{COOEt})_{10}$, is obtained as a thick, yellowish oil.

Ethyl monochloromalonate reacts with ethyl sodiopropionylpentacarboxylate, yielding *ethyl butonylheptacarboxylate*, which distils at 280—285° under 130 mm. pressure, with partial decomposition. The *chloro-derivative* is a thick, almost colourless oil, sp. gr. 1.169 at 15° (water at 15° = 1).

Ethyl octoïntesserakaïdecacarboxylate,



it obtained by the action of ethyl sodiobutonylheptacarboxylate on the ethyl salt of chlorobutonylheptacarboxylate; it is a thick, nearly colourless oil. N. H. M.

Methylamides and Ethylamides of Trichloroacetic and Trimethylacetic Acid and their Action on Nitric Acid. By A. P. N. FRANCHIMONT and E. A. KLOBBIE (*Rec. Trav. Chim.*, 6, 234—246).—*Trichloroacetomethylamide* is prepared by mixing ethyl trichloroacetate with a slight excess of an aqueous 30 per cent. solution of methylamine. It crystallises from ether in white crystals melting at 105—106°. Nitric acid slowly acts on it with evolution of gas; no nitro-compound is formed. The ethylamide is also slowly decomposed by nitric acid, with evolution of nitrous oxide.

Trichloroacetodimethylamide is obtained by adding drop by drop an ethereal solution of trichloroacetic chloride to a well-cooled ethereal solution of dimethylamine, and is purified by distillation in a vacuum. It is a colourless liquid, which solidifies when cooled by means of ether and carbonic anhydride, and is slightly soluble in water. Sp. gr. = 1.441 at 15°. It is not decomposed by nitric acid, even when heated with it.

Trichloroacetodiethylamide forms large, transparent crystals, melts at 27°, and is very sparingly soluble in water. It decomposes when distilled in a vacuum (compare Cloëz, *Abstr.*, 1887, 1098). It is not attacked by nitric acid when kept in contact with it for 24 hours. *Trimethylacetamide*, prepared by heating ammonium trimethylacetate at 220—230°, crystallises from water in long, slender needles, melts at 153—154°, and boils at about 212° under 766.5 mm. pressure. It is at once decomposed by nitric acid at the ordinary temperature with evolution of nitrous oxide.

Methylamine trimethylacetic acid, $(\text{CMe}_3\cdot\text{COOH})_2\text{NH}_2\text{Me}$, is formed when trimethylacetic acid and methylamine are heated at 150° for 10—12 hours. It forms slender needles, melts at 81°, boils at 173—175° under 750 mm. pressure, dissolves readily in water, ether, and methyl alcohol, sparingly in light petroleum, and is hygroscopic.

Trimethylacetomethylamide is prepared by the action of trimethylacetic chloride on methylamine both dissolved in ether. It melts at 91°, sublimes at a lower temperature, boils at 203—204° under 759.1 mm. pressure, and is readily soluble in water, alcohol, and ether. It is at once attacked by nitric acid with evolution of nitrous oxide.

Trimethylacetethylamide, prepared in a manner similar to the methylamide, crystallises well, melts at 49°, boils at 203—204° under 765 mm. pressure, and is readily soluble in water, alcohol, and ether. It is decomposed by nitric acid, but not completely in 24 hours.

Trimethylacetodimethylamide is a colourless liquid, boiling at 185—186° under 754 mm. pressure, and is very soluble in water. Sp. gr. = 0.912 at 17°. It does not give off gas when treated with nitric acid at the ordinary temperature, but yields nitrodimethylamine.

Trimethylacetodiethylamide is a colourless liquid, very readily soluble in water. Sp. gr. 0.891 at 15°. It boils at 203°. Neither this substance nor the dimethylamide could be obtained quite pure. It does not evolve gas when treated with nitric acid, but a trace of nitro-diethylamine seems to be formed after 24 hours. N. H. M.

Methylamides and Ethylamides of Heptylic Acid. By A. P. N. FRANCHIMONT and E. A. KLOBBIE (*Rec. Trav. Chim.*, **6**, 247—250).—The compounds are prepared by heating heptylic acid with the amines at 230° for five hours, dissolving the products in ether, and adding potassium carbonate; after 24 hours, water is added, the ethereal solution separated, dried by potassium carbonate, and distilled. They are colourless liquids, slightly soluble in water. The *methylamide* is a thick liquid of a slight odour, boiling at 265·5—266·5° under 758 mm. pressure. Sp. gr. = 0·895 at 15°. The *ethylamide* melts at 5—6°, and boils at 267·5—268·5° under 767 mm. pressure. The *dimethylamide* boils at 242·5—243·5° under 758·5 mm. pressure. Sp. gr. = 0·894 at 15°. The *diethylamide* boils at 257·5—258·5° under 765 mm. pressure. Sp. gr. = 0·881 at 15°.

Both monalkylamides give off gas when treated with nitric acid. The dimethylamide gives off a little gas, nitrodimethylamine being formed. The diethylamide is decomposed by nitric acid with liberation of heptylic acid.
N. H. M.

Formation of Amidobutyric Acid by the Action of Ammonia on Crotonic Acid. By ENGEL (*Compt. rend.*, **106**, 1677—1679).—25 grams of crotonic acid was mixed with 200 c.c. of a solution of ammonia containing 100—115 milligram-molecules in 10 c.c., and the mixture was heated in sealed tubes at 100—105° for 10 hours; the product was then evaporated with lead oxide, and the lead removed from the solution by means of hydrogen sulphide. Amidobutyric acid forms white non-deliquescent crystals, very soluble in water, and soluble in alcohol, from which it is precipitated by ether. Its solution dissolves many metallic oxides; for example, cupric oxide forms a deep blue solution, which yields large crystals of the composition $(C_4H_7NO_2)_2Cu + 4H_2O$. These crystals are only slightly efflorescent, and do not become anhydrous at 100°.

This amidobutyric acid is much more soluble than the α -derivative, and is probably the β -acid, a view which is supported by the fact that its copper salt is also much more soluble than the copper salt of α -amidobutyric acid as described by Heintz.
C. H. B.

Amides of Carbonic Acid. By F. EMICH (*Monatsh.*, **9**, 378—394).—The following compounds, cyanamide, biuret, amidodicyanic acid, diacyanodiamide, diacyanodiamidine, melamine, ammeline, biuret dicyanamide, melem, ammelide, cyameluric acid, melam, mellon, and mellon hydride are readily decomposed into carbonic anhydride and ammonia with fixation of the elements of water. The decomposition was effected by heating about 0·2 gram of the substance with moderately dilute sulphuric acid; in some cases the sulphuric acid can be replaced by phosphoric acid or alkalis, or by water alone at a sufficiently high temperature.

Compounds such as fulminic acid, fulminuric acid, and isuretin are not decomposed in this simple manner.
F. S. K.

Urethane and some of its Derivatives. By E. MULDER (*Rec. Trav. Chim.*, **6**, 169—198).—Urethane dissolved in alcohol is con-

verted by alcoholic potash at the ordinary temperature into potassium isocyanate, $\text{NK}\cdot\text{CO}$; no potassium carbamate is formed as intermediate product (compare Arth, *Bull. Soc. Chim.*, **41**, 334). The same reaction takes place when potassium ethoxide is used.

Potassium acts on urethane dissolved in ether with evolution of hydrogen and formation of potassium isocyanate.

Ethyl sodiocarbamate, $\text{NHNa}\cdot\text{COOEt}$, obtained by adding sodium to an ethereal solution of urethane, and washing the white precipitate with absolute ether, is very hygroscopic, and dissolves readily in alcohol. The alcoholic solution deposits crystals of sodium isocyanate.

Alcoholic potash, or soda, in presence of water, converts urethane into potassium or sodium carbonate.

Ammonium carbamate, prepared by Basaroff's method, when treated with alcoholic potash, yields a gelatinous compound, probably potassium carbamate, which in presence of a little water is converted into potassium hydrogen carbonate.

When alcoholic solutions of urethane, potash, and mercuric chloride are mixed, the compound $\text{NHg}\cdot\text{COOEt}$ is obtained as a gelatinous mass; when dried it can be readily powdered, and is nearly colourless. In presence of water, the powder swells up, but without dissolving. A small amount of potassium chloride is formed in the reaction.

Sandmeyer's ethyl chlorimidocarbonate (Abstr., 1886, 611) may be considered as formed by the direct union of normal ethyl cyanate and ethyl hypochlorite.

N. H. M.

Reaction Product of Phosphorus Pentasulphide and Carbamide. By C. v. KUTSCHIG (*Monatsh.*, **9**, 406—413).—The compound $\text{C}_2\text{H}_5\text{N}_3\text{PS}_2\text{O}_2$ is obtained by heating an intimate mixture of carbamide (1 part) and phosphorus pentasulphide (2 parts) at $80-90^\circ$ for 20 to 30 minutes, and treating the product with water. It crystallises from hot water in shining, monosymmetric crystals, is rather easily soluble in water, sparingly in alcohol, and shows a strongly acid reaction. About one-third of its nitrogen is evolved as nitrogen when it is treated with bromine, and the same quantity is evolved as ammonia when it is boiled with potash. Biuret, and a compound containing both sulphur and phosphorus, are obtained when it is heated with lead oxide. It is decomposed into hydrogen sulphide, ammonia, and phosphoric acid, when heated with moderately concentrated hydrochloric acid, but in absence of air it yields ammonia, hydrogen sulphide, and hypophosphorus acid. A silver salt, $\text{C}_2\text{H}_5\text{AgN}_3\text{PS}_2\text{O}_2$, is obtained when an aqueous solution, acidified with acetic acid, is precipitated with silver acetate. When an aqueous solution of 1 gram of the substance is slowly added to an ammoniacal solution of 2.54 grams of silver nitrate, a white unstable salt, $\text{C}_2\text{H}_5\text{Ag}_3\text{N}_3\text{PS}_2\text{O}_2$, is formed.

F. S. K.

Urëids, and their Reactions with Nitric Acid. By A. P. N. FRANCHIMONT (*Rec. Trav. Chim.*, **6**, 213—223).—It was previously shown that carbamide as well as its methyl-derivatives are readily

decomposed by nitric acid at the ordinary temperature (*Rec. Trav. Chim.*, **2**, 96 and 330; **3**, 216), generally behaving like the amides and methylamides of the fatty acids. In the present paper, the behaviour of other carbamide-derivatives towards nitric acid is described.

Hydantoic acid, acetylcarbamide, and bromoacetylcarbamide, when treated with nitric acid, give off a gas consisting of 1 vol. of carbonic anhydride and 2 vols. of nitrous oxide; biuret gives equal vols. of the two gases, whilst oxaluric acid yields a mixture of carbonic anhydride, nitrous oxide, carbonic oxide, and nitrogen.

Hydantoin and lactylcarbamide are converted into nitro-derivatives; acetonylcarbamide is not attacked by nitric acid.

Parabanic and dimethylparabanic acids, dimethylmalonureid and alloxan are not attacked by nitric acid. Barbituric acid and isosuccinylcarbamide yield nitro-derivatives.

The above results show that when the carbamide forms a closed chain with an acid residue, it loses its amidic character, whilst, when an open chain is formed, the compound is at once decomposed by nitric acid. This is confirmed by the behaviour of allantoin, 1 mol. of which when treated with nitric acid gives off 1 mol. of carbonic anhydride and 2 mols. of nitrous oxide.

Ethylenecarbamide, when treated with nitric acid, yields a nitro-derivative, whilst ethylenedicarbamide is decomposed, yielding equal vols. of carbonic anhydride and nitrous oxide; the disappearance of the amidic character is therefore due to the formation of a closed chain, and not to the presence of carbonyl-groups. Acetylenecarbamide yields a dinitro-derivative.

When ethylenecarbamide, $\text{CHM} < \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} > \text{CO}$, is treated with nitric acid, a mixture of equal vols. of carbonic anhydride and nitrous oxide is evolved; this may be due to the splitting up of an unstable nitro-derivative formed as intermediate product with carbamide and a nitro-hydrocarbon. It is, however, mentioned that the constitution of ethylenecarbamide is not so conclusively established as that of the other compounds examined. Uric acid dissolves in nitric acid with slight development of heat and evolution of carbonic anhydride and nitrous oxide. Caffeine is attacked slowly, and theobromine still more slowly. Xanthine also gives off gas. N. H. M.

Aspartic Acids. By ENGEL (*Compt. rend.*, **106**, 1734—1737).—The author has previously shown (*Abstr.*, 1887, 917) that fumaric and maleic acids unite directly with ammonia to form aspartic acid. The identity or otherwise of the aspartic acids thus formed is of very great interest in connection with the isomerism of the generating acids. Four varieties of aspartic acid were compared, namely: (A) formed by the combination of fumaric acid with ammonia; (B) formed by the combination of maleic acid with ammonia; (C) the acid obtained by Desaignes' method; and (D) the active acid obtained from asparagin. The combination of fumaric and maleic acids with ammonia takes place at 100° in presence of water. At this temperature aspartic acid is not decomposed by water, and

maleic acid is not transformed into fumaric acid. The molecular weights of maleic and fumaric acid as determined by Raoult's method are identical, and the molecular weights of the four aspartic acids as determined by the same method are also identical. The three acids, A, B, and C have the same degree of solubility which is expressed by the equation $\gamma = 517 + 21.693t - 0.165t^2 + 0.0079t^3$. The solubility of the active acid is different, the equation in this case being $\gamma = 372 + 14.1t - 0.18124t^2 + 0.0053t^3$. Cupric aspartate prepared from the four acids always crystallises with 9 mols. H_2O , but the crystals from the active acid D are pale-blue needles, whereas the crystals from the three acids A, B, C, whilst identical among themselves, are darker and less definite than those from the acid D.

When the active acid is exposed to the air, it soon becomes covered with mould, and if some of this mould is transferred to solutions of the other three acids, they soon acquire a lœvorotatory power. Advantage is taken of the insolubility of the active aspartic acid in a saturated solution of the inactive acid to isolate the active acids formed by the action of the mould, and when the new active acids are mixed with an equal weight of the active acid from asparagin, they produce an inactive acid identical with the three acids, A, B, and C.

From these results it follows that fumaric and maleic acids combine with ammonia to form the same inactive aspartic acid.

C. H. B.

Ethyl Telluride. By A. MARQUARDT and A. MICHAELIS (*Ber.*, **21**, 2042—2046).—*Triethyl telluride chloride*, $TeEt_3Cl$, is obtained by adding an ethereal solution of tellurium tetrachloride, drop by drop, to a similar solution of zinc ethide; it crystallises from alcohol in colourless plates, melts at 174° , dissolves readily in alcohol, sparingly in ether. It deliquesces when exposed to air; when treated with moist silver oxide, the hydroxy-derivative is formed; this yields with hydriodic acid Becker and Cahours' iodide, $TeEt_3I$ (*Ann. Chim. Phys.* [5], **10**, 50), melting at $90-92^\circ$. When the triethyl-compound is heated with an excess of zinc ethide at $100-110^\circ$, butane and diethyl telluride are formed. The latter is obtained as a reddish oil boiling at 140° ; the pure diethyl telluride from potassium telluride boils at $137-138^\circ$, not 98° (Wöhler, *Annalen*, **35**, 111, and Heeren, *Jahresber.*, 1861, 565).

Triethyl telluride bromide is a white, deliquescent substance, melts at 162° , dissolves readily in water and alcohol, and is insoluble in ether.

N. H. M.

Alkyl-derivatives of Bismuth. By A. MARQUARDT (*Ber.*, **21**, 2035—2042; compare Abstr., 1887, 802).—Hydrogen sulphide reacts with methylbismuthine oxide and with dimethylbismuthine oxide in alcoholic solution, with formation of voluminous orange-coloured precipitates readily soluble in ammonium sulphide. The compounds could not be purified and are probably represented by the formulæ $BiMeS$ and Bi_2Me_4S . When heated, bismuth sulphide is formed.

Triisobutylbismuthine, $Bi(C_4H_9)_3$, prepared in a manner similar to

the trimethyl-compound (*loc. cit.*) by adding bismuth bromide to zinc isobutyl, forms a heavy, colourless liquid having a slight odour of butyl-compounds; it fumes in air and burns on filter-paper with a dark yellow flame. It boils at 160—162° under 74 mm. pressure with partial decomposition.

Diisobutylbismuthine bromide, $\text{BiBr}(\text{C}_4\text{H}_9)_2$, obtained by adding bromine to a solution of the tributyl-compound in light petroleum, forms white, tabular crystals readily soluble in alcohol. It burns when exposed to air.

Isobutylbismuthine dibromide, $\text{BiBr}_2\cdot\text{C}_4\text{H}_9$, is formed when isobutylbismuthine and bismuth bromide in molecular proportion are dissolved together in dry ether. It melts at 124°, crystallises in honey-coloured prisms readily soluble in alcohol and glacial acetic acid, rather sparingly in ether; when exposed to air, it remains unchanged.

Diisobutylbismuthine hydroxide is a yellow, crystalline compound which inflames when exposed to air.

Triisoamylbismuthine, $\text{Bi}(\text{C}_5\text{H}_{11})_3$, is a colourless, slightly fuming liquid which boils at 190—200° under 70 mm. pressure with partial decomposition.

Diisoamylbismuthine bromide forms white crystals readily soluble in alcohol, less so in ether; it inflames in air.

Isoamylbismuthine dibromide is obtained by mixing ethereal solutions of bismuth bromide and triisoamylbismuthine, and on evaporating the ether separates as a honey-yellow oil, which solidifies to a pulverulent mass when cooled; it is insoluble in light petroleum, soluble in alcohol and ether. No halogen compounds of the alkyl-derivatives of bismuth could be obtained. N. H. M.

Condensation of Glyoxal with Ethylmalonate and Acetoacetate. By M. POLONOWSKY (*Annalen*, 246, 1—32).—*Ethyl dihydroxybutanetetra-carboxylate*, $\text{CH}(\text{COOEt})\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{COOEt})_2$, is obtained in the form of a thick syrup by the action of a concentrated aqueous solution of zinc chloride on a mixture of glyoxal (1 mol.) and ethyl malonate (2 mols.). When a mixture of glyoxal and ethyl acetoacetate is treated with a concentrated aqueous solution of zinc chloride at the ordinary temperature, a syrupy liquid is produced which is extracted with ether. The product is separated into two distinct portions by treatment with sodium hydroxide. The portion soluble in alkali contains *methylfurfurancarboxyacetic* or "*sylvanecarboxyacetic*" acid, $\text{O} < \begin{smallmatrix} \text{C}(\text{CH}_2\cdot\text{COOH})\cdot\text{CH} \\ \text{CMe}=\text{C}(\text{COOH}) \end{smallmatrix} >$. This acid is best prepared by hydrolysis of the crude product at the ordinary temperature. After three or four days, the alkaline solution is acidified; the acid is then deposited in crystals which are purified by recrystallisation from alcohol and afterwards from hot water. The pure acid melts at 207°, decomposes at 250°, crystallises in needles, and dissolves freely in alcohol and also in alkalis and alkaline carbonates. The *ammonium salt*, $\text{C}_6\text{H}_6\text{O}_5(\text{NH}_4)_2 + \frac{1}{2}\text{H}_2\text{O}$, is deposited in microscopic needles on passing ammonia gas into an alcoholic solution of the acid. The *barium salt*, $\text{C}_6\text{H}_6\text{O}_5\text{Ba} + 2\text{H}_2\text{O}$, forms transparent needles. The

silver salt contains 1 mol. H_2O . It is much more soluble in hot than in cold water.

When an alcoholic solution of the acid is saturated with hydrogen chloride, the normal and the acid ethereal salts are formed. The mixture of the two methyl salts is separated by treatment with a solution of sodium carbonate, in which the normal ether is insoluble and the acid salt soluble. $\text{C}_6\text{H}_5\text{O}(\text{COOMe})_2$ is an uncrystallisable liquid. The acid salt, $\text{COOH}\cdot\text{C}_6\text{H}_5\text{O}\cdot\text{COOMe}$, crystallises in needles and melts at 98° . It yields crystalline barium and silver salts. The latter has the formula $\text{COOMe}\cdot\text{C}_6\text{H}_5\text{O}\cdot\text{COOAg}$. The acid ethylic salt, $\text{COOH}\cdot\text{C}_6\text{H}_5\text{O}\cdot\text{COOEt}$, melts at 76° . The dicarboxylic acid is converted into *sylvanacetic* acid, $\text{C}_4\text{OHMe}\cdot\text{CH}_2\cdot\text{COOH}$, by exposure to a temperature somewhat above its melting point. The new acid melts at $137\text{--}138^\circ$. It dissolves freely in alcohol and is volatile in a current of steam. The silver salt, $\text{C}_7\text{H}_7\text{O}_3\text{Ag} + \frac{1}{2}\text{H}_2\text{O}$, is slightly soluble in hot water. The barium salt crystallises with $4\frac{1}{2}$ mols. H_2O .

That portion of the original condensation product of glyoxal and ethyl acetoacetate which is insoluble in alkalis, separates in the course of time into a thick oil and a small quantity of a crystalline compound, both having the composition $\text{C}_{14}\text{H}_{18}\text{O}_6$. The crystals melt at 139° and are sparingly soluble in the ordinary solvents. The oil consists of diethylsylvanecarboxyacetoacetate, $\text{COOEt}\cdot\text{C}_4\text{OHMe}\cdot\text{CHAc}\cdot\text{COOEt}$. It is miscible with alcohol, ether, benzene, and chloroform.

Sylvanecarboxyacetic acid is converted into acetonylacetone on heating it at 200° with water containing a minute quantity of hydrochloric acid.
W. C. W.

Thiophen. By B. PAWLEWSKI (*Ber.*, **21**, 2141—2142).—From determinations of its vapour-density at various temperatures, the author concludes that thiophen is not decomposed when heated at $336\text{--}340^\circ$. The critical temperature was found to be $317\cdot3^\circ$, and the critical pressure $47\cdot7$ atmospheres, from which Van der Waal's constants are calculated to be $a = 0\cdot04145$, $t = 0\cdot00566$, and $v = 0\cdot01698$. (Compare R. Schiff, *Abstr.*, 1885, 971.)

F. S. K.

Constants of Benzene. By B. LACHOWICZ (*Ber.*, **21**, 2206—2210).—The discordant results obtained by many experimenters in the determinations of the constants of benzene, are probably due to the air which is dissolved by benzene in considerable quantities, and is very difficult to get rid of. The author found the boiling point to be $80\cdot39^\circ$ at 760 mm. pressure and the melting point $5\cdot42^\circ$. Some benzene melts at $4\cdot84^\circ$ because of the air which it contains; benzene containing air can be cooled to $-4\cdot2^\circ$ before it solidifies, whereas benzene free from air cannot be cooled below $+3^\circ$ or sometimes even $+5^\circ$ without solidifying. The sp. gr., reduced to 4° and a vacuum, is $0\cdot87270$ at $24\cdot27^\circ$, whereas benzene which is not freed from air has a sp. gr. $0\cdot87451$ at the same temperature.

In the following table the mean coefficient of expansion for the temperature t° is given in the column α . Column v gives the volume calculated from the coefficients of expansion, Kopp's value for 5°

being taken as the starting point. The column $\left(\frac{g}{4^\circ}\right)$ gives the sp. gr. calculated from the sp. gr. at $24\cdot27^\circ$ reduced to 4° and a vacuum. Column $\left(\frac{1}{g}\right)$ gives the specific and column $\left(\frac{m}{g}\right)$ the molecular volume ($C = 11\cdot97$).

t° .	a .	t° .	v .	$\frac{g}{4^\circ}$.	$\frac{1}{g}$.	$\frac{m}{g}$.
—	—	0	1·00000	0·89408	1·11846	87·04
5—6	0·0012185	5	00589	88885	12505	87·53
6—10	11319	6	00712	88776	12641	87·66
10—15	11561	10	01168	88376	13153	88·06
15—20	11634	15	01752	87868	13807	88·56
20—25	12097	20	02344	87360	14468	89·08
25—30	12371	25	02468	87255	14607	89·19
30—35	12384	30	03102	86718	15316	89·74
35—40	12512	35	03740	86184	16030	90·29
40—45	12749	40	04389	85649	16756	90·86
45—50	13428	45	05055	85106	17502	91·44
50—55	13599	50	05760	84539	18289	92·05
55—60	12417	55	06479	83968	19093	92·68
60—65	13433	60	07140	83450	19833	93·25
65—70	13455	65	07860	82893	20673	93·88
70—75	13469	70	08586	82339	21449	94·51
75—84	13429	75	09317	81784	22273	95·15
—	—	80	10051	81239	23094	95·79
—	—	80·39	—	81196	23159	95·84

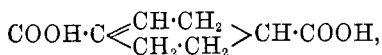
F. S. K.

Physical Constants of Benzene. By A. HORSTMANN (*Ber.*, **21**, 2211—2222).—The author discusses the various results which have been obtained in determinations of the heat of combustion of various saturated and unsaturated hydrocarbons, including benzene, and concludes that in physical properties benzene is intermediate between the saturated and unsaturated compounds, a conclusion which Baeyer has already drawn from a study of the chemical properties.

F. S. K.

Constitution of Benzene. By A. V. BAEYER (*Annalen*, **245**, 103—190; compare *Trans.*, 1887, 208).—The reduction products of terephthalic acid have no longer the character of benzene-derivatives, the di- and tetra-hydro-acids behaving like unsaturated, whilst the hexahydro-acid behaves like a saturated fatty acid. The latter acid yields a mono- and a di-bromo-derivative in which the bromine atoms taken up the α -positions: $\text{COOH}\cdot\text{CBr}\langle\text{CH}_2\cdot\text{CH}_2\rangle\text{CH}\cdot\text{COOH}$ and $\text{COOH}\cdot\text{CBr}\langle\text{CH}_2\cdot\text{CH}_2\rangle\text{CBr}\cdot\text{COOH}$. The derivative obtained by the addition of hydrogen bromide to tetrahydroterephthalic acid has the constitution $[\text{Br} = 2]$.

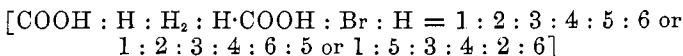
Tetrahydroterephthalic acid has the constitution



which is proved as follows: (1.) The acid combines with 1 mol. of bromine, yielding a saturated acid not identical with the two known dibromohexahydro-acids in which the bromine is in the para-position; when reduced, the bromine is displaced by hydrogen. (2.) In the hydrobromide of the tetrahydro-acid, the bromine is in the β -position, as two acids different from it in which the bromine are in the α -position are formed by the bromination of the hexahydro-acid, and a third is not conceivable. (3.) The formation from the dibromide of the tetrahydro-acid of a hydroxy-acid which yields tetrabromopyrocatechol when treated with bromine.

Tetrahydroterephthalic acid dibromide, when boiled with aqueous soda, yields the same dihydro-acid as that obtained by reduction. The dihydro-acid combines with 2 mols. of bromine, yielding a saturated acid from which the same dihydro-acid can be regenerated by heating it with an alkali. It also yields a dibromide. This, when treated with bromine, yields a lactone ether which is reduced by zinc-dust and acetic acid to the hydrogen alkyl salt of the dihydro-acid, and is therefore derived from a tetrabromide in which two pairs of bromine-atoms are attached to adjacent carbon-atoms. The constitution of the dibromide of the tetrahydro-acid and of the dihydro-acid is expressed by the formulæ $\text{COOH}\cdot\text{CBr}\begin{matrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CHBr}\cdot\text{CH}_2 \end{matrix}\text{CH}\cdot\text{COOH}$ and $\text{COOH}\cdot\text{C}\begin{matrix} \text{CH}\cdot\text{CH}_2 \\ \text{CH}\cdot\text{CH} \end{matrix}\text{CH}\cdot\text{COOH}$.

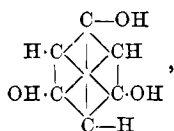
The dibromides of tetra- and di-hydroterephthalic acids both give up 2 mols. HBr when treated with alkalis; the former reaction is readily explained by the production of two double unions, whilst the adoption of this explanation in the second case would involve the assumption that in the elimination of 1 mol. of HBr a monobromide of the constitution



is formed. The bromine-atoms must therefore be eliminated along with hydrogen-atoms from the ortho-para- or from the meta-meta-positions. For this reason, the author concludes that the constitution of terephthalic acid cannot be explained by any theory hitherto suggested; this view is supported by a comparison of the stability on the one hand of terephthalic acid, and on the other its di- and tetra-hydro-derivatives. Whereas the latter have the properties of unsaturated fatty acids, terephthalic acid is exceedingly stable, and it follows that terephthalic acid cannot in the ordinary sense contain double combinations. Claus' diagonal formula would give a satisfactory explanation of the behaviour of terephthalic acid, but must be rejected as not harmonising with the constitution of dihydro-terephthalic acid.

The formula for benzene which the author now adopts is that first suggested by Kekulé (*Annalen*, **137**, 158), but afterwards given up

owing to the difficulty of explaining the trivalency of carbon which it involved, a difficulty now got over by the representation of atoms in space. If it is assumed that the six carbon-atoms of benzene, in consequence of the attraction of free affinities, turn on the axes (formed by the sides of the hexagon) in such a way that their direction tends inwards towards the plane of the ring, the six points of attack lie symmetrically within the ring, and may paralyse one another, so as to be practically unavailable, or in other words, carbon in benzene is trivalent. A figure is given showing the relative position of the carbon- and hydrogen-atoms. The carbon-atoms are represented by equidistant points, and the three bonds of each carbon-atom by three lines forming three angles of 120° , so that the inner bonds meet to one point in the middle. The fourth valency forms nearly a right angle to the plane of the drawing. It is probable that all the hydrogen-atoms are on one side of the plane of the ring, as when mellitic acid is reduced a maleinoid hexahydro-acid is formed: all the carboxyl-groups are therefore on the same side, and hence also all the hydrogen-atoms of benzene. In the model of benzene, two groups of opposing forces are represented, the central valencies tending to draw the atoms towards the middle point, and the peripheral bonds striving to widen out the ring. In benzene these forces are in equilibrium, but as soon as the two central valencies become (by means of reducing agents) united to hydrogen, the equilibrium is destroyed, and the tension of the peripheral bonds (now in excess), expanding the ring, causes the four remaining valencies to associate to double unions. The best example of this is phloroglucinol—



which when treated with hydroxylamine yields a derivative of hexamethylene.

The geometrical isomerism of hexahydroterephthalic acid depends on the presence of asymmetric carbon-atoms. This isomerism is, however, to be distinguished from that which depends on the presence of two asymmetric carbon-atoms in open chains, as in the case of tartaric acid. Whilst this acid retains its geometrical isomerism when one of the carbon-atoms loses its asymmetric character by the displacement of hydroxyl by hydrogen, this is not the case with hexahydroterephthalic acid. On displacing one of the carboxyl-groups of the hexahydro-acid by hydrogen, hexahydrobenzoic acid is formed which no longer contains asymmetric carbon and also no longer shows geometrical isomerism. The isomerism of hexahydroterephthalic acids corresponds exactly with that of fumaric and maleic acids. The one acid (corresponding with fumaric acid) is sparingly soluble in water, crystallises in prisms and sublimes when heated. The other forms large crystals, dissolves readily in water, and melts at 160° . It may therefore be safely assumed that in the readily soluble

hexahydro-acid both carboxyl-groups are situated on the same side of the plane of the ring.

Terephthalic acid is best prepared by gradually adding dry bromine (2 mols.) to 100 grams of paraxylene contained in a reflux apparatus and heated at 150° . The product is digested in a water-bath with an alcoholic solution of potassium acetate. The acetate is heated on a water-bath with 1 litre of water, 500 grams of aqueous soda (sp. gr. = 1.22), and treated gradually with 4.5 litres of 10 per cent. permanganate solution, more being afterwards added, if necessary. After being heated for three hours, it is filtered, treated with alkali, the solution heated in a water-bath and gradually acidified. In this way, the terephthalic acid is made to separate in needles. The methyl salt dissolves in 300 parts of hot water, and is sparingly soluble in methyl alcohol, more readily in ethyl alcohol. It forms rhombic plates (brachypinakoid and primary pyramid); $a:b:c = 0.84281:1:3.0826$. Paraxylene forms monoclinic crystals: $a:b:c = 2.32:1:2.34$; $\beta = 69\frac{1}{2}^{\circ}$.

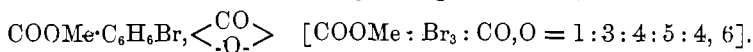
Dihydroterephthalic acid (contrary to a previous statement, *loc. cit.*) is readily obtained by dissolving 50 grams of terephthalic acid in a mixture of 120 grams of aqueous soda (sp. gr. = 1.22), and 400 c.c. of water, and adding 3.5 kilos. of 3 per cent. sodium amalgam and sufficient water to prevent the separation of sodium salts. A small amount of paratoluylic acid is formed, to get rid of which the crude acids are converted into ethyl salts which are easily separated from each other. It resembles terephthalic acid in appearance as well as in solubility. It does not melt, but sublimes with partial decomposition into terephthalic acid. The *methyl salt* prepared similarly to methyl terephthalate, crystallises in monoclinic plates ($a:b:c = 1.52:1:2.79$; $\beta =$ about 74°), dissolves in hot alcohol, less in hot water, and melts at 130° . When the methyl salt is heated with alcoholic potash, an intense yellow coloration is produced. The salt is less readily saponified than that of terephthalic acid; on treating it with alcoholic potash and then with acid, an ether acid is formed which melts at 225° .

In determining the behaviour of substances towards permanganate solution, it is best to use sodium carbonate instead of soda, as then no manganate is formed in the conversion of the permanganate into the brown oxide. Terephthalic acid is not changed in the cold by permanganate and only very slowly when warmed. Di- and tetra-hydro-terephthalic acids are immediately oxidised in the cold; the hexahydro-acid is not oxidised in the cold but rather quickly when warmed. The halogen-derivatives behave similarly. The method is useful to separate all unsaturated from saturated acids. The results obtained with a number of acids are given.

Dihydroterephthalic acid dihydrobromide, $C_8H_{10}Br_2O_4$, is prepared by heating methyl dihydroterephthalate with aqueous hydrogen bromide (saturated at 0°) for three hours at 120° . It is a crystalline powder. When treated with silver oxide, carbonic anhydride is evolved and an acid—probably dihydrobenzoic acid—melting at about 115° is formed. The *methyl salt*, $C_{10}H_{14}Br_2O_4$, crystallises in thin monoclinic plates; $a:b:c = 1.5477:1:3.0027$; $\beta = 85^{\circ} 17'$. It melts at 166° . It is much more stable than the acid, and is scarcely changed when heated

with acetic acid and silver acetate at 130° ; at 160° , ethyl dihydrophthalate is formed. When reduced, both the acid and the salt yield the hexahydro-derivative.

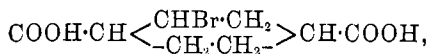
Methyl dihydroterephthalate dibromide, $C_{10}H_{12}Br_2O_4$, is obtained by adding 35 grams of bromine dissolved in 100 grams of chloroform in three portions to a solution of 20 grams of methyl dihydroterephthalate in 200 grams of chloroform, taking care to avoid too great rise of temperature. After a quarter of an hour the solution is cooled down, decolorised with sulphurous acid, washed with potassium carbonate solution, and dried with potassium carbonate. The crude salt, which contains the methyl dihydroterephthalate or terephthalate, is saponified with a mixture of sulphuric and acetic acids; the *methyl hydrogen salt* thus obtained forms colourless plates. This is reconverted into the dimethyl salt in the usual manner. It melts at 90° . When reduced with glacial acetic acid and zinc-dust, it yields ethyl dihydroterephthalate; cold alcoholic potash converts it into ethyl hydrogen terephthalate. The *free acid* obtained by heating the methyl salt with hydrobromic acid on a water-bath for 8 to 10 hours, crystallises from hot water in small rhombohedra. When methyl dihydroterephthalate dibromide is treated with an excess of bromine, it is converted into the *tribromolactone ether of hexahydroterephthalic acid*,



This forms colourless plates, melts at $187-188^{\circ}$, dissolves sparingly in ether, more readily in methyl and ethyl alcohols, and still more in warm chloroform and glacial acetic acid. When the lactone ether is reduced, hydrogen methyl dihydroterephthalate is formed. It is probable that in the preparation of the lactone the tetrabromide of methyl dihydroterephthalate, $[Br \cdot COOMe : (HBr)_3 : H \cdot COOMe : H_2 = 1 : 2 : 3 : 6 : 4 : 5]$, is formed as intermediate product. The above experiments show that dihydroterephthalic acid contains two ethylene-like combinations. Tetrahydroterephthalic acid (Abstr., 1887, 370) yields sparingly soluble *barium* and *potassium salts*, the former crystallising in characteristic triclinic plates. The methyl salt forms long, lustrous needles, like caffeine, and dissolves very readily in most solvents; it has no odour and shows no fluorescence when pure. The rose-coloured precipitate previously obtained with sodium ethoxide is also due to an impurity. The tetrahydro-acid unites with bromine and with hydrogen bromide more readily than the dihydro-acid. The dibromide, $C_8H_{10}Br_2O_4$, is best obtained by adding bromine to the solution of the acid in phosphorus pentachloride, decolorising the product with sulphurous acid, and recrystallising it from water. It dissolves sparingly in water, readily in ether. When boiled with aqueous potash, it yields the dihydro-acid, and when reduced with zinc-dust and acetic acid it is converted into the tetrahydro-acid. The experiments previously made (*loc. cit.*) to determine the position of the bromine-atoms were repeated and confirmed. The methyl salt of the dibromide is prepared from the methyl salt of the tetrahydro-acid; the product contains crystals of two forms and consists probably of two geometric isomerides; the larger crystals (which are in excess)

melt at 81°. When the methyl salt is reduced, or is heated with alcoholic potash, the tetrahydro-acid is formed.

Tetrahydroterephthalic acid hydrobromide,



is prepared by heating 1 gram of the tetrahydro-acid with 7.5 c.c. of hydrobromic acid (saturated at 0°) for one day at 100° and one day at 125°. To remove traces of unchanged tetrahydro-acid, the product is treated with permanganate. It has about the same solubility in water as the tetrahydro-acid, but is much more readily soluble in ether. It is converted by aqueous or alcoholic potash into the tetrahydro-acid and by zinc-dust and glacial acetic acid into the hexahydro-acid. When warmed with water and silver oxide, an acid is obtained, probably tetrahydrobenzoic acid. *Methyl tetrahydroterephthalate hydrobromide* forms monoclinic crystals; $a:b:c = 2.9050:1:1.3694$; melts at 94—95°, and is sparingly soluble in ether and light petroleum. When reduced, the methyl salt of fumaroid hexahydroterephthalic acid is formed.

In the preparation of the above hydrobromide, a considerable amount of an acid readily soluble in water is formed. This contains bromine, and goes over into the tetrahydro-acid on distilling off the hydrobromic acid. It is isolated by nearly neutralising the acid solution with sodium carbonate, saturating with sodium chloride, and extracting with ether. It forms a syrup which afterwards becomes crystalline. The acid seems to be a geometrical isomeride of the hydrobromide just described, derived from maleinoid hexahydroterephthalic acid, as when treated with zinc-dust and glacial acetic acid, it yields the *cis*-hexahydro-acid, whilst the ordinary hydrobromide yields scarcely anything but the ordinary hexahydro-acid.

Hexahydroterephthalic acid (fumaroid acid) is best prepared from tetrahydroterephthalic acid dibromide. It crystallises from water in groups of prisms, like ammonium chloride, dissolves readily in alcohol and acetone, sparingly in ether, in 75 parts of boiling water, and in 1162 parts of water at 16.5°. The *alkali* and *barium salts* are readily soluble; the *calcium salt* forms sparingly soluble quartz-like crystals; the *copper*, *lead*, and *silver salts* are sparingly soluble. The methyl salt forms triclinic plates or prisms, having a slight odour of ethyl malonate, soluble in 200 parts of hot water.

Cis-hexahydroterephthalic acid (maleinoid acid) is best obtained by reducing the readily soluble hydrobromide of the tetrahydro-acid, and can also be prepared from the dibromohexahydro acid obtained by substitution. It is readily soluble in ether, chloroform, and alcohol, sparingly in cold water, but much less so than the fumaroid acid. It melts at 162°. When heated with hydrochloric acid for three hours at 180°, it is converted into the ordinary acid. The salts are more soluble than those of ordinary hexahydroterephthalic acid, and more difficult to obtain crystalline.

Hexahydroterephthalic acid behaves towards bromine like a saturated fatty acid, yielding substitution products without opening the ring; the free acid is with difficulty attacked, the acid chloride

readily, especially in presence of phosphorus compounds, the bromine taking up the α -position to the carboxyl-group.

1. 4-Dibromohexahydrotetraphthalic acid is obtained together with 1, 4 dibromo-cis-hexahydrotetraphthalic acid by treating the hexahydro-acid with phosphorus pentachloride, and heating the product with bromine for three hours at 150° . It forms a granular crystalline precipitate, readily soluble in ether and alcohol, almost insoluble in water. When reduced, it yields both hexahydro-acids and is converted by alcoholic potash into dihydrotetraphthalic acid. The methyl salt crystallises in large, strongly refractive, monoclinic prisms; $a:b:c = 2.2742:1:0.89288$; $\beta = 87^{\circ} 54'$. It melts at 150° .

1. 4-Dibromo-cis-hexahydrotetraphthalic acid crystallises in extremely slender needles, rather readily soluble in cold water, very readily in alcohol, ether, and acetone. The methyl salt crystallises in hair-like needles, melts at 68° , dissolves very readily in alcohol and ether, less in light petroleum. The anilide crystallises in long prisms or in hair-like needles, and melts at 200° with decomposition.

1-Bromohexahydrotetraphthalic acid is prepared in a manner exactly similar to the dibromo-acid, except that rather more than half the amount of bromine is used and the mixture is heated for five hours in a water-bath. The product of the reaction, containing unchanged hexahydro-acid, two bromo- and two dibromo-acids, is dissolved in sodium carbonate, filtered and diluted so that the volume amounts to 1 litre (6 grams of acid having been used). It is acidified, kept for 24 hours, when the fumaroid dibromo-acid separates, filtered, saturated with sodium chloride, and extracted 10 times with ether. The extract is shaken with sodium carbonate, and the aqueous solution, after being freed from dissolved ether, is acidified. The fumaroid bromo-acid separates first as a granular precipitate, then the cis-dibromo-acid; when no more of the latter separates, the whole is quickly filtered, as the greater part of the cis-monobromo-acid is still in solution. The precipitate is washed with cold water, and the residue, after being freed from hexahydro-acid, is converted into methyl salts. The mixed methyl salts of the fumaroid and cis-monobromo- and the fumaroid dibromo-hexahydro-acids are dissolved in light petroleum, and the crystals which separate dissolved in methyl alcohol; the salt of the dibromo-acid separates first, then that of the fumaroid bromo-acid. This crystallises in monoclinic plates; $a:b:c = 0.34724:1:0.46944$; $\beta = 82^{\circ} 50'$; and melts at $70-71^{\circ}$. The free acid was not obtained pure. When boiled with aqueous soda, it yields the same tetrahydro-acid as does the fumaroid 2-monobromo-acid.

1-Bromo-cis-hexahydrotetraphthalic acid separates very slowly from its aqueous solution in short, spear-formed crystals melting at about 205° . The methyl salt could not be crystallised. The anilide forms hair-like needles, rather soluble in hot glacial acetic acid.

When tetrahydrotetraphthalic acid hydrobromide (2-bromohexahydrotetraphthalic acid) is converted into the chloride, and treated with bromine, a dibromohexahydro-acid, quite distinct from those obtained by substitution from the hexahydro-acid, is formed. It could not be identified with the dibromide of the tetrahydro-acid, as the methyl salt could not be crystallised, which is probably due to the

presence of geometrical isomerides. When reduced with zinc and glacial acetic acid, it is converted into the tetrahydro-acid. The paper concludes with a reply to Geuther (this vol., p. 579). N. H. M.

Preparation and Oxidation-products of Nitrocymene. By H. G. SÖDERBAUM and O. WIDMAN (*Ber.*, **21**, 2126—2129).—Nitrocymene [$\text{Me} : \text{NO}_2 : \text{Pr} = 1 : 2 : 4$] is best prepared by dropping a little more than the calculated quantity of nitric acid (sp. gr. 1.4) mixed with $1\frac{1}{2}$ times its weight of concentrated sulphuric acid, into the cymene contained in a well-cooled retort, the whole being shaken during the process. The temperature is kept at $20\text{--}25^\circ$ at first, and afterwards raised to 40° . The mixture is then shaken until it becomes cold, water added, and the nitro-derivative washed with soda, then with water, and distilled with steam. The product contains paratolyl methyl ketone, which can be separated by fractional distillation with steam, the ketone distilling first. The pure nitro-compound is a slightly yellow oil with an aromatic odour; it yields cymidine (carvadyamine) when reduced with tin and hydrochloric acid. *Cymidine hydrochloride*, $\text{C}_{10}\text{H}_{15}\text{N}\cdot\text{HCl}$, crystallises in flat, shining needles. The *sulphate*, $(\text{C}_{10}\text{H}_{15}\text{N})_2\cdot\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$, loses its water at 80° . Ortho-nitroparahydroxyisopropylbenzoic acid and terephthalic acid are formed when nitrocymene is oxidised with alkaline permanganate.

F. S. K.

Cholesterin. By F. REINITZER (*Monatsh.*, **9**, 421—441).—The bromo-derivative of acetylcholesterin has the formula $\text{C}_{27}\text{H}_{45}\text{Br}_2\text{OAc}$, and, as it is an additive product, the formula of cholesterin is $\text{C}_{27}\text{H}_{46}\text{O}$, but it is probable that several homologous cholesterins occur in the animal organism.

Melted cholesteryl acetate, $\text{C}_{27}\text{H}_{45}\text{OAc}$, shows the colour phenomena before and not after solidifying, as is stated by Raymann (*Abstr.*, 1887, 926). It exists in three modifications: the first is obtained by crystallising it from solvents; when the crystals are warmed, they become clouded before melting, owing to formation of a mass of crystals of the third modification. The second modification is obtained in the form of spherocrystals when the melted substance is quickly cooled; if xylene is added, the single crystals can be obtained: they are large, thin, monosymmetric leaves, and behave like the first modification when heated. The third modification is formed when either of the other two is heated or when the melted substance is cooled slowly. Cholesteryl acetate is decomposed when heated above its melting point, but a small portion sublimes unchanged. It is not decomposed by water. (Compare Raymann, *loc. cit.*)

Bromocholesteryl acetate is sparingly soluble in alcohol, but readily soluble in ether, and crystallises from alcoholic ether in long, thin, shining plates. It forms monosymmetric crystals melting at 118° (corr.), and asymmetric crystals melting at 115.8° (corr.); it turns yellow when melted, and cannot be again obtained in crystals. It yields cholesterin when reduced with sodium amalgam in ethereal solution, but some other compound appears to be also formed. It gives a yellow, amorphous compound when treated with potash. Cholesteryl benzoate, $\text{C}_{27}\text{H}_{45}\text{OBz}$, melts at 146.6° (corr.) to a turbid

liquid. It exists in three modifications:—The first modification is obtained by crystallisation from solvents; the crystals belong to the tetragonal system, melt at a higher temperature than the other two modifications, and remain clear when heated. The second modification is formed when the melted substance is quickly cooled; it melts at a slightly lower temperature than the third modification, and forms flat needles or small leaves belonging to the rhombic system. The third modification is obtained when the melted substance is cooled slowly; it forms thin, broad leaves. After heating to 178.5° , cholesterol benzoate shows similar colour phenomena on cooling to those observed in the case of the acetate.

Nitrocholesterin is obtained when a hot, saturated glacial acetic acid solution of cholesterol is treated with nitric acid—sp. gr. 1.54. It is a reddish-yellow, tasteless, odourless, amorphous compound, melts at $93-94^{\circ}$ with decomposition, and is readily soluble in alcohol, ether, chloroform, benzene, glacial acetic acid, ammonia, and alkalis, but insoluble in water.

F. S. K.

Alkyl-derivatives of Benzylamine. Reduction of Amarine.

By H. ZAUNSCHIRM (*Annalen*, **245**, 279—288; compare Fischer, this vol., p. 50).—*Benzylidene-ethylamine*, $\text{CHPh}\cdot\text{NEt}$, prepared by mixing benzaldehyde with an aqueous 33 per cent. solution of ethylamine, is a clear oil of a penetrating odour, boils at 195° (uncorr.) at 749 mm. pressure, is readily soluble in ether and alcohol, and is decomposed by dilute acids into its constituents. When reduced by sodium amalgam, *ethylbenzylamine*, $\text{CH}_2\text{Ph}\cdot\text{NHet}$, is formed. This boils at $191-194^{\circ}$ (uncorr.) under 740 mm. pressure, has an odour like that of benzylamine, dissolves readily in alcohol and ether, and reacts strongly alkaline. The salts dissolve readily in water and alcohol. The *platinochloride*, $(\text{C}_6\text{H}_{13}\text{N})_2\cdot\text{H}_2\text{PtCl}_6$, crystallises in orange-coloured needles.

Benzylidenemethylamine, $\text{CHPh}\cdot\text{NMe}$, resembles the ethylamine compound. *Methylbenzylamine*, $\text{CH}_2\text{Ph}\cdot\text{NHMe}$, boils at $184-185^{\circ}$ (uncorr.) under 749 mm. pressure; the *platinochloride* was prepared.

Propyl-, isobutyl-, and amyl-benzylamine are strong bases and have an odour of fish; the salts dissolve readily in water and alcohol; the nitroso-derivatives are oils.

Benzylidenepropylamine, $\text{CHPh}\cdot\text{NHPr}$, boils at $208-210^{\circ}$ (uncorr.) under 744 mm. pressure. *Propylbenzylamine*, $\text{CH}_2\text{Ph}\cdot\text{NHPr}$, boils at 210° under 741 mm. pressure; the *platinochloride* crystallises in large, orange-coloured prisms.

Benzylideneisobutylamine, $\text{CHPh}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CHMe}_2$, boils at $217-218^{\circ}$ (uncorr.) under 735 mm. pressure. *Isobutylbenzylamine*, $\text{C}_{11}\text{H}_{17}\text{N}$, boils at $217-220^{\circ}$ (uncorr.) under 741 mm. pressure.

Amylbenzylamine, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{C}_5\text{H}_{11}$, boils at 240° (uncorr.) under 745 mm. pressure; the *platinochloride* crystallises well.

Ethylbenzylthiocarbamic acid, $\text{CH}_2\text{Ph}\cdot\text{NEt}\cdot\text{CSSH}$, is obtained by treating an alcoholic solution of ethylbenzylamine with carbon bisulphide; after boiling for several hours, the carbon bisulphide and alcohol are distilled off. It melts at 114° , dissolves readily in benzene and carbon bisulphide, sparingly in ether and light petroleum.

When amarine is reduced by sodium amalgam, a compound melting

at 163° is obtained which, when heated with dilute sulphuric acid, is converted into benzaldehyde and a base melting at 108—113°.

Lophine is reduced by sodium amalgam with formation of an isomeric amarine. (Kohler, *Dissertation*, Erlangen, 1888.)

N. H. M.

Ammonia-derivatives of Cumaldehyde. By C. UEBEL (*Annalen*, **245**, 289—310).—*Cuminylaniline*, $C_6H_4Pr\cdot CH_2\cdot NHPh$, is prepared by dissolving cuminaniline (Schiff, *Annalen*, Suppl. **3**, 357) in about 10 parts of alcohol and gradually adding rather more than the calculated amount of 3 per cent. sodium amalgam, the whole being kept cool if necessary; the reaction is completed by heating for a short time on the water-bath in a reflux apparatus. The product is treated with a little water, most of the alcohol distilled off, and the residue steam distilled. The yellow oil is dissolved in ether, dried, freed from ether, and made to crystallise by means of a freezing mixture. It crystallises from alcoholic ether in well-formed, triclinic plates, melts at 41·5°, and dissolves very readily in alcohol and ether. The *hydrochloride* crystallises from dilute alcohol in slender, lustrous needles; the *nitroso-derivative*, $C_6H_4Pr\cdot CH_2\cdot NPh\cdot NO$, crystallises from absolute alcohol in long, yellowish needles melting at 94·5° (uncorr.).

Cumintoluidine, $C_6H_4Pr\cdot CH\cdot N\cdot C_6H_4Me$, is obtained by adding paratoluidine to an alcoholic solution of cumaldehyde; the mixture is warmed a little on a water-bath, treated with alcohol until a clear solution is obtained, and left to crystallise. It forms large, lustrous, bright-yellow, transparent plates, probably triclinic, and melts at 51°. It does not form salts, but is decomposed when heated with alkalis or dilute acids.

Cuminytoluidine, $C_6H_4Pr\cdot CH_2\cdot NH\cdot C_6H_4Me$, prepared by reducing cumintoluidine with sodium amalgam, crystallises in well-formed, clear, triclinic plates, melts at 36° (uncorr.), and distils above 210° in a vacuum without decomposition. It is very readily soluble in alcohol and ether, insoluble in water. The *hydrochloride* crystallises from hot water in slender, white needles, very readily soluble in alcohol. The *nitroso-derivative* crystallises from alcoholic ether in lustrous, bright-yellow, prismatic needles melting at 67°.

Cuminamidophenol, $C_6H_4Pr\cdot CH\cdot N\cdot C_6H_4\cdot OH$, is formed when amido-phenol is added to an alcoholic solution of cumaldehyde. It crystallises in well-formed, lustrous, rhombic prisms, of a moss-green colour, melts at 183° with decomposition, and, when dry, remains unchanged.

Cuminylamidophenol, $C_6H_4Pr\cdot CH_2\cdot NH\cdot C_6H_4\cdot OH$, separates in greyish-white plates when carbonic anhydride is passed through the solution of the sodium salt; it melts with decomposition at 107—108° (uncorr.), dissolves very readily in alcohol and ether, but cannot be easily recrystallised owing to its instability. The *hydrochloride* forms white plates readily soluble in alcohol and in hot water; the *nitroso-compound* is a yellowish-brown, crystalline substance, readily soluble in alcohol and ether.

Cuminamidodimethylaniline, $C_6H_4Pr\cdot CH\cdot N\cdot C_6H_4\cdot NMe_2$, obtained by the action of cumaldehyde on freshly prepared amidodimethylaniline (Wurster, *Abstr.*, 1879, 626), crystallises in intensely yellow, slender

needles, melts at 100.5° (uncorr.), is readily soluble in alcohol and ether, and insoluble in water.

Cuminylamidodimethylaniline, $C_6H_4Pr \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot NMe_2$, crystallises in large, well-formed, prismatic plates, melts at 39° (uncorr.), and dissolves readily in alcoholic ether. The *hydrochloride* separates from the alcoholic solution in long, slender needles of a silky lustre. The *nitroso-derivative* crystallises in long, gold-coloured needles, melts at 87° , and dissolves readily in alcohol and ether.

Hydrocuminamide, $C_6H_7 \cdot C_6H_4 \cdot CH(N \cdot CH \cdot C_6H_4Pr)_2$ (Borodin, this Jour., 1874, 273, and Sieveking, *Annalen*, **106**, 259), is prepared by passing dry ammonia through a solution of cumaldehyde in an equal volume of absolute alcohol and much absolute ether for several hours under pressure. The vessel containing the mixture is well closed, and kept for some time in a freezing mixture, when hydrocuminamide separates in groups of needles. The ether is poured off, and the solution as well as the undissolved portion put into a desiccator which is pumped out several times and kept in a cold place. It forms stellate groups of needles, melts at 65° , and is very readily soluble in alcohol, less so in ether. When pure, it remains unchanged if kept in closed vessels, but becomes yellow and resinous when exposed to moist air. When reduced with sodium amalgam, it is converted into isopropylbenzylamine and diisopropylbenzylamine, which are separated from each other by distillation with steam.

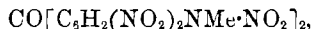
Isopropylbenzylamine, which is found in the distillate, is identical with Rossi's cumylamine (compare Goldschmidt and Gessner, *Abstr.*, 1887, 1039). It boils at $226-228^{\circ}$ (uncorr.). When exposed to the air, it absorbs carbonic anhydride very readily, yielding a *carbonate* which crystallises in large, transparent plates. The *platinochloride* crystallises from alcohol, in which it is readily soluble, in gold-coloured plates.

Diisopropylbenzylamine, $NH(CH_2 \cdot C_6H_4Pr)_2$, forms white, compact crystals, melts at 168° , boils without decomposition at $280-300^{\circ}$ under 100 mm. pressure. It is readily soluble in alcohol, insoluble in water. The *hydrochloride* crystallises in large, lustrous plates, very readily soluble in alcohol; the *platinochloride* forms slender, yellow needles. The *nitrosamine*, $NO \cdot N(CH_2 \cdot C_6H_4Pr)_2$, crystallises in long, pale-yellow needles, readily soluble in alcohol, sparingly in ether.

N. H. M.

Nitramines derived from Alkyl Aromatic Diamines. By P. VAN ROMBURGH (*Rec. Trav. Chim.*, **6**, 251-254).—When methylmetaphenylenediamine is boiled with fuming nitric acid, *trinitrophenylenedimethyldinitramine*, $C_6H(NMe \cdot NO_2)_2(NO_2)_3$, is formed.

Tetranitrodimethyldinitramidobenzophenone,



is obtained by boiling tetramethyldiamidobenzophenone with nitric acid (sp. gr. = 1.40 or 1.42); it forms pale-yellow crystals which decompose at 210° . Boiling phenol acts on it with formation of *tetranitrodimethyldiamidobenzophenone*, $CO[C_6H_2(NO_2)_2 \cdot NMe]_2$. This is yellow, and melts at 225° with decomposition.

When dinitrodimethylaniline is treated with nitric acid (sp. gr. = 1.36) in the cold, two isomeric trinitrodimethylanilines, melting at 196° and 154° respectively, are formed. (Compare *Rec. Trav. Chim.*, **2**, 105.) Boiling fuming nitric acid converts the above di- and trinitro-derivatives into a yellow crystalline substance, probably $\text{OH}\cdot\text{C}_6\text{H}(\text{NO}_2)_3\cdot\text{NMe}\cdot\text{NO}_2$.
N. H. M.

Thio-derivatives of some Secondary and Tertiary Amines.

By E. HOLZMANN (*Ber.*, **21**, 2056—2071).—*Oxydimethylaniline*, $\text{O}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, is formed when an alcoholic solution of 1 mol. of thiodimethylaniline in presence of ammonia is boiled with an ammoniacal alcoholic solution of silver nitrate for about one hour. It crystallises in stellate groups of needles melting at 119°, and is soluble in alcohol, ether, and benzene, readily soluble in acids. The *platinochloride*, $\text{O}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{H}_2\text{PtCl}_6$, is a bright yellow, microcrystalline substance, sparingly soluble in hot alcohol and water. The *picrate* is a yellow, crystalline precipitate, melts at 150°, dissolves readily in hot alcohol and benzene; when heated it detonates.

Thiodiethylaniline, $\text{S}(\text{C}_6\text{H}_4\cdot\text{NEt}_2)_2$, is prepared by dissolving diethylaniline (4 mols.) in light petroleum, and gradually adding to the well-cooled solution a solution of sulphur dichloride (1 mol.) in light petroleum. It crystallises from alcohol in yellowish needles, melts at 79.5—80°, is insoluble in water, readily soluble in warm alcohol, ether, benzene, and glacial acetic acid. The *platinochloride* is a yellow, flaky precipitate, insoluble in water, very sparingly soluble in alcohol. The *picrate* forms sulphur-coloured, slender, lustrous needles, melts at 175°, and is sparingly soluble.

Oxydiethylaniline, $\text{O}(\text{C}_6\text{H}_4\cdot\text{NEt}_2)_2$, crystallises in colourless needles, melts at 89°, is insoluble in water, readily soluble in warm alcohol, ether, and benzene. When pure, it is stable when exposed to air. The *platinochloride* is a yellow, flaky, sparingly soluble substance. The *picrate* forms slender, yellow crystals, melts at 174°, and is sparingly soluble.

Dithiodiphenylamine, $\text{S}_2<\text{C}_6\text{H}_4>\text{NH}$, is formed when a solution of 10 grams of diphenylamine in an excess of light petroleum is well-cooled and treated with a solution of 2.5 grams of sulphur chloride in light petroleum. The greenish product is dissolved in benzene and boiled with benzene in a reflux apparatus. It crystallises in slender, yellow needles melting at 59—60°. It dissolves readily in warm alcohol, ether, and benzene, and is insoluble in water.

Thiodiphenylamine (Bernthsen, *Abstr.*, 1884, 595) is obtained by treating a well-cooled solution of diphenylamine in benzene with a similar solution of sulphur dichloride. It crystallises in almost colourless plates, melts at 180°, and boils at 370°.

Methylthiodiphenylamine, $\text{S}<\text{C}_6\text{H}_4>\text{NMe}$, prepared by the action of sulphur dichloride on methyl diphenylamine, forms slender, bright yellow needles, melts at 78—79°, and decomposes when heated above 360°. It is insoluble in water, rather soluble in warm benzene, sparingly soluble in boiling alcohol and ether. The compound is an

isomeride of that prepared by Bernthsen (*loc. cit.*) from thiodiphenylamine, methyl iodide, and methyl alcohol (compare Mohlau and Krohn, this vol., p. 364).

When thiodimethylaniline is heated with 10 parts of freshly reduced copper at 300° , dimethylaniline is formed. Thiodiphenylamine, when heated with copper, yields carbazole (Goske, *Abstr.*, 1887, 372), whilst dithiodiphenylamine yields diphenylamine. Methylthiodiphenylamine (from thiodiphenylamine) is converted by copper into carbazole; methylthiodiphenylamine from methyldiphenylamine yields no carbazole but methyldiphenylamine.

N. H. M.

Action of Aniline on Quinonephenylimide and Diphenylparazophenylene. Synthesis of Dianilidoquinoneanil and Azophenine. By E. v. BANDROWSKI (*Monatsh.*, 9, 414—420; compare this vol., p. 943).—Quinonephenylimide and aniline react very readily, producing dianilidoquinoneanil and parahydroxydiphenylamine; the yield of the former is almost theoretical.

Diphenylparazophenylene and aniline yield azophenine and diphenylparaphenylenediamine. The quantity of azophenine produced is 59.9 per cent. of the diphenylparazophenylene employed.

F. S. K.

Action of Paratoluidine and of Aniline on Phloroglucinol. By G. MINUNNI (*Ber.*, 21, 1984—1991).—*Triparatolyltriamidobenzene*, $C_6H_3(NH \cdot C_7H_7)_3$, is formed when a mixture of paratoluidine and phloroglucinol is heated at 200 — 210° . It crystallises in slender, white needles melting at 186 — 187° , is very sparingly soluble in cold alcohol, sparingly soluble in hot alcohol, but relatively easily soluble in warm benzene or ether. It is soluble in acids; a cold concentrated sulphuric acid solution turns bluish-green and finally black when heated, and with sodium nitrite gives a bluish-green coloration which changes to brown on adding a considerable quantity of the reagent. The base forms two hydrochlorides. The *monacid* salt, $C_{27}H_{27}N_3 \cdot HCl$, is obtained in the form of a yellowish, seemingly amorphous precipitate when dry hydrogen chloride is passed into a benzene solution of the base. The *diacid* salt, $C_{27}H_{27}N_3 \cdot 2HCl$, crystallises in small needles when a concentrated hydrochloric acid solution is evaporated slowly. Both salts are decomposed by an excess of water. The *platinochloride*, $(C_{27}H_{27}N_3)_2 \cdot H_2PtCl_6$, is a yellow, crystalline compound which is insoluble in ordinary solvents and is decomposed by boiling water. The triacetyl-derivative, $C_6H_3(NAc \cdot C_7H_7)_3$, crystallises from warm alcohol in microscopic leaves, melts at 192 — 193° , is readily soluble in benzene, sparingly soluble in ether, and insoluble in water. The *tribenzoyl*-derivative, $C_6H_3(NBz \cdot C_7H_7)_3$, crystallises from boiling alcohol in microscopic prisms melting at 281 — 282° . It is almost insoluble in cold ether, only very sparingly soluble in warm ether, and sparingly in alcohol and benzene. It is soluble in concentrated sulphuric acid and is precipitated unchanged by water.

Triphenyltriamidobenzene, $C_6H_3(NHPh)_3$, prepared by heating phloroglucinol with aniline at 210° , crystallises from alcohol in slender, white needles, melting at 193° . It is sparingly soluble in cold, but readily soluble in hot alcohol or benzene, and still more readily

soluble in ether. Ammonia precipitates it unchanged from the hydrochloric acid solution. A concentrated sulphuric acid solution becomes violet-red and finally black when heated; in a sulphuric acid solution, sodium nitrite produces a violet-red coloration which changes to yellowish-brown on adding a considerable quantity of the reagent. The *hydrochloride*, $C_6H_3(NHPh)_3 \cdot HCl$, is a yellow powder, melts below 100° , and is decomposed by warm water. The *platinochloride*, $(C_{24}H_{21}N_3)_2 \cdot H_2PtCl_6$, is yellow, crystalline, insoluble in ether and benzene, and sparingly soluble in boiling alcohol, and melts at about 250° with decomposition. The *triacetyl-derivative*, $C_6H_3(NPhAc)_3$, crystallises from boiling alcohol in microscopic needles, melts at $172-173^\circ$, is sparingly soluble in cold, but very readily soluble in hot alcohol or ether. The *tribenzoyl-derivative*, $C_6H_3(NPhBz)_3$, crystallises from alcoholic benzene in white, microscopic needles melting above 300° . It is soluble in hot, but only sparingly soluble in cold alcohol or benzene. F. S. K.

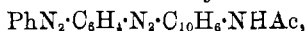
Disazo-compounds. By R. NIETZKI and J. DIESTERWEG (*Ber.*, **21**, 2143—2147).—Diazoazobenzene combines with aniline to form a yellowish-red diazoamido-compound melting at 119° . When this substance is dissolved in aniline, mixed with aniline hydrochloride, and kept for about 24 hours at $40-50^\circ$, the greater part is converted into ordinary amidoazobenzene, but a small quantity of amidodisazobenzene is also formed. The latter is isolated by precipitating with hydrochloric acid, dissolving the precipitate in alcoholic ammonia, and reprecipitating with hydrochloric acid. The mixture of hydrochlorides is decomposed with alkali and the bases converted into the acetyl-derivatives. The acetylamidodisazobenzene, which is more sparingly soluble, is separated from the acetylamidoazobenzene by partial recrystallisation from alcohol. The yield is about 1 per cent.

Acetylamidodisazobenzene, $PhN_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NHAc$, crystallises from hot alcohol or glacial acetic acid in orange-yellow plates, melts at 227° , and gives a dark green coloration with concentrated sulphuric acid.

Amidodisazobenzene is obtained by boiling the acetyl-derivative with alcoholic potash. It crystallises in yellow plates, melts at 170° , is very sparingly soluble in alcohol, and dissolves in concentrated sulphuric acid, forming a dark red solution which turns a deep blue when a few drops of water are added.

Disazobenzene, $PhN_2 \cdot C_6H_4 \cdot N_2 \cdot Ph$, is formed when the amido-derivative is treated with potassium nitrite and sulphuric acid in alcoholic solution and the mixture boiled for some time. It crystallises from ether or benzene in yellowish-red, well-defined needles, melts at 98° , and dissolves in concentrated sulphuric acid, forming a yellow solution.

α -Amidonaphthalenedisazobenzene, $PhN_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_7 \cdot NH_2$, prepared by mixing solutions of diazoazobenzene hydrochloride and α -naphthylamine hydrochloride, crystallises from glacial acetic acid in green plates which melt at 170° , and give a deep blue colour with concentrated sulphuric acid. The *acetyl-derivative*,



crystallises in yellowish-red plates, melts at 275° , and dissolves in concentrated sulphuric acid, forming a green solution.

Naphthalenedisazobenzene, $\text{PhN}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_7$, prepared by treating amidonaphthalenedisazobenzene with sodium nitrite and sulphuric acid in alcoholic solution and boiling the mixture, crystallises in yellowish-brown plates, melts at 143° , and gives a green solution with concentrated sulphuric acid.

β -Amidonaphthalenedisazobenzene, prepared similarly to the α -compound, crystallises from alcohol in red needles, melts at 164° , and gives a blue solution with sulphuric acid. The *acetyl*-derivative crystallises in red plates, melts at 206° , and dissolves in concentrated sulphuric acid with a red colour.

F. S. K.

Carbodiimides of the Aromatic Series and Phenylhydrazine.

By R. WESSEL (*Ber.*, **21**, 2272—2278).—*Carbodiphenylaminehydrazide*, $\text{N}_2\text{HPh} \cdot \text{C}(\text{NHPh})_2$, is obtained when carbodiphenylamide and phenylhydrazine in molecular proportion are heated together at 120° for half an hour. It crystallises from boiling alcohol in slightly reddish needles, melts at 204° , and turns red on exposure to the air. It is readily soluble in boiling alcohol, benzene, chloroform, &c., moderately soluble in ether, but almost insoluble in light petroleum. The salts are colourless and crystalline. The *hydrochloride*, $\text{C}_{19}\text{H}_{18}\text{N}_4 \cdot \text{HCl}$, crystallises from warm alcohol in needles, and is insoluble in ether and light petroleum, but readily soluble in water, dilute hydrochloric acid, and boiling alcohol. The *platinochloride*, $(\text{C}_{19}\text{H}_{18}\text{N}_4)_2 \cdot \text{H}_2\text{PtCl}_6$, crystallises from warm alcohol in yellow, lustrous needles, is almost insoluble in water, and decomposes when heated. The *sulphate*, $\text{C}_{19}\text{H}_{18}\text{N}_4 \cdot \text{H}_2\text{SO}_4$, separates from alcoholic ether in white, crystalline crusts, and is soluble in boiling alcohol and water but almost insoluble in ether.

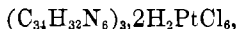
Carbodiparatolylaminehydrazide, $\text{N}_2\text{HPh} \cdot \text{C}(\text{NH} \cdot \text{C}_7\text{H}_7)_2$, prepared by heating a mixture of carbodiparatolylimide with phenylhydrazine in molecular proportion at 160 — 170° , crystallises from warm alcohol in pale-red needles, melts at 138° , and behaves towards solvents like the preceding compound. The *platinochloride*, $(\text{C}_{21}\text{H}_{22}\text{N}_4)_2 \cdot \text{H}_2\text{PtCl}_6$, is very similar to the corresponding salt described above.

The compound, $2\text{C}_{13}\text{H}_{10}\text{N}_2 \cdot \text{C}_6\text{H}_5\text{N}_2$, is formed when carbodiphenylaminehydrazide (1 mol.) is heated at 185° for half an hour with phenylhydrazine (1 mol.). It separates from boiling alcohol in white crystals, melts at 200° , is only moderately soluble in boiling alcohol or ether, more readily in boiling benzene, and insoluble in light petroleum. The *hydrochloride*, $(\text{C}_{32}\text{H}_{28}\text{N}_6)_3 \cdot 4\text{HCl}$, crystallises in white plates, and is readily soluble in hot water, dilute hydrochloric acid, and boiling alcohol. The *platinochloride*, $(\text{C}_{32}\text{H}_{28}\text{N}_6)_3 \cdot 2\text{H}_2\text{PtCl}_6$, is decomposed when gently heated.

The compound, $2\text{C}_{15}\text{H}_{11}\text{N}_2 \cdot \text{C}_6\text{H}_5\text{N}_2$, is obtained by heating 1 mol. of carboditolylaminehydrazide with 1 mol. of phenylhydrazine at 190 — 195° . It crystallises from alcohol in plates, melts at 163° , and is only very sparingly soluble in boiling ether. The *hydrochloride*, $(\text{C}_{36}\text{H}_{36}\text{N}_6)_3 \cdot 4\text{HCl}$, separates from a hot hydrochloric acid solution of

the base in white crusts. The *platinochloride*, $(C_{36}H_{36}N_6)_3 \cdot 2H_2PtCl_6$, is decomposed when heated gently.

The compound $C_{13}H_{20}N_2 \cdot C_{15}H_{14}N_2 \cdot C_6H_8N_2$ is obtained when carbodiphenylaminehydrazide is heated with carbodiparatolyimide. It crystallises from boiling alcohol in white needles, melts at 128° , and is sparingly soluble in warm alcohol or ether. The *hydrochloride*, $(C_{34}H_{32}N_6)_3 \cdot 4HCl$, crystallises in colourless plates, and is readily soluble in hot water and boiling alcohol. The *platinochloride*,



decomposes when heated gently.

The compound $C_6H_8N_2 \cdot C_{13}H_{10}N_2 \cdot C_7H_5NS$, prepared by heating carbodiphenylaminehydrazide with phenylthiocarbimide at 190° , crystallises from boiling alcohol in white needles, melts at 175° , and is moderately soluble in boiling alcohol or ether. F. S. K.

Action of Carbamide on Hydrazines. By A. PINNER (*Ber.*, 21, 2329—2331).—The compound obtained by heating phenylsemicarbazide (Pinner, this vol., p. 687) is *diphenylurazine*, $C_{14}H_{12}N_4O_2$; when boiled with acetic anhydride for a few seconds, it yields an *acetyl-derivative*, $C_{14}H_{11}N_4O_2Ac$, which separates from benzene in small, nodular crystals melting at 173° . The *diacetyl-derivative*, $C_{14}H_{10}N_4O_2Ac_2$, obtained by heating diphenylurazine with acetic anhydride and sodium acetate, crystallises in stellate needles, melts at 153° , and is readily soluble in alcohol and benzene, but insoluble in water and light petroleum.

Ethyldiphenylurazine, $C_{14}H_{11}N_4O_2Et$, prepared by heating an alcoholic solution of the urazine with potash (2 mols.) and ethyl iodide (2 mols.), crystallises in large, shining prisms, melts at 137° , and is readily soluble in alcohol, but insoluble in ether.

The constitution of diphenylurazine is probably $\begin{matrix} NPh \cdot NH \cdot CO \\ < & NPh \cdot CO \cdot NH > \end{matrix}$. F. S. K.

Xanthogallol. By C. A. THEURER (*Annalen*, 245, 327—356).—Xanthogallol is very stable towards oxidising agents, and can be crystallised from strong nitric acid; it is very readily reduced. When heated at 130° it sublimes with partial decomposition.

When 5 grams of xanthogallol dissolved in 25 grams of glacial acetic acid is cooled and treated with 5 grams of aniline diluted with glacial acetic acid, the compound $C_{18}H_4Br_{11}O_6(NHPh)_4$ is formed. This crystallises in large, greenish-yellow prisms and melts at 204 — 206° .

The *paratoluidine-derivative*, $C_{18}H_4Br_{11}O_6(NH \cdot C_7H_7)_4$, is more readily soluble in alcohol than the aniline compound.

The *chloromethoxy-derivative*, $C_{18}H_4Br_{11}Cl_3O_3(OMe)_3$, is formed when hydrogen chloride is passed through a cooled solution of 4 grams of xanthogallol in 80 grams of methyl alcohol. It crystallises in large, well-formed, colourless crystals, melts at 86° , dissolves readily in methyl alcohol, alcohol, and glacial acetic acid, and is almost insoluble in water. It does not react with aniline, and is decomposed by dilute alkalis.

The *chlourethoxy-derivative*, $C_{18}H_4Br_{11}Cl_3O_3(OEt)_3$, crystallises in large prisms of a vitreous lustre, melting at 75° ; it is more difficult to saponify than the methoxy-derivative.

The *bromomethoxy-derivative*, $C_{18}H_4Br_{11}O_3(OMe)_3$, prepared in a manner similar to the chloromethoxy-compound, using hydrogen bromide, forms colourless prisms melting at 113° . When boiled with dilute soda, filtered, and treated with excess of strong hydrochloric acid, the compound $C_6H_2Br_4O_2(OMe)_2$ is obtained. The latter melts at 105° , and is very readily soluble in alcohol, ether, glacial acetic acid and benzene, less soluble in water. When dissolved in methyl alcohol, and the solution saturated with hydrogen chloride, the compound $C_6HBr_4Cl(OMe)_4$ is formed. This forms large, hard prisms of vitreous lustre, melting at 77° .

The *aniline-derivative of xanthogallol*, $C_6H_2Br_4O_4Me_2 \cdot NH_2Ph$, is obtained by treating the acid $C_6H_2Br_4O_2(OMe)_2$ with aniline; it forms white crystals.

In the preparation of the ethoxy-derivative from xanthogallol, the compound $C_{18}H_4Br_{11}Cl_3O_8$ is obtained. It forms large, yellow crystals, melts at 104° , and dissolves readily in alcohol and benzene.

Trihydroxyxanthogallol crystallises with 7 mols. H_2O in long, matted needles melting at 72° ; the anhydrous crystals melt at 131° . The *aniline-derivative*, $C_{18}H_7Br_{11}O_8(NH_2Ph)_8$, crystallises in small, white needles, very readily soluble in alcohol. The *toluidine-derivative*, $C_{18}H_7Br_{11}O_8(NH_2 \cdot C_6H_7)_8$, forms small, white plates.

When xanthogallol is suspended in water and treated with soda, it gradually dissolves, whilst the liquid becomes milky and gradually deposits a pulverulent precipitate mixed with oily drops. It is extracted with ether, and the oil so obtained dissolved in alcohol. On evaporating the alcohol, crystals of the *hexabromodihydrobenzene*, $C_6H_2Br_6$, separate. This forms long, white prisms, melts at 139° , and is sparingly soluble in alcohol and light petroleum, more soluble in benzene; it is very stable, and is not attacked by alkalis or by sulphuric and nitric acids. Alcoholic potash acts on it, eliminating hydrogen bromide. The alkaline solution, from which the neutral substance was extracted, contains the sodium salt of an acid. The *free acid* forms slender, white needles, and melts at 124° ; the *barium salt*, $C_6H_2Br_2BaO_3 + 3H_2O$, was prepared.

Xanthogallol may be considered as derived from 3 mols. of tri-bromopyrogallol by the elimination of 3 mols. H_2O and addition of 2 mols. of bromine and 1 mol. of hydrogen bromide. It would then have the formula $C_6HOBr_2 < \begin{smallmatrix} O \cdot C_6H_2OBr_3 \\ O \cdot C_6HOBr_3 \end{smallmatrix} > O$. This formula explains the various reactions of xanthogallol, and the formation of derivatives containing six carbon-atoms. The constitution of these compounds and of trihydroxyxanthogallol is also discussed.

N. H. M.

Acetopropylbenzene, Acetocumene, and their Derivatives.

By O. WIDMAN (*Ber.*, 21, 2224—2233).—*Paracetopropylbenzene*, $C_6H_4Pr^a \cdot COMe$, prepared by treating propylbenzene with acetic chloride in presence of aluminium chloride, is a colourless, mobile

liquid with a strong aromatic odour. It boils at 259° (765 mm.), and distils with slight decomposition.

Paracetocumene, $C_6H_4Pr^{\beta} \cdot CMe$, prepared in like manner, boils at $252-254^{\circ}$ (756 mm.).

Acetopropylbenzeneoxime, $C_6H_4Pr^{\alpha} \cdot CMe \cdot NOH$, obtained by warming an alcoholic solution of acetopropylbenzene with hydroxylamine, crystallises from light petroleum in large, well-defined, colourless, very readily soluble plates melting at $43-44^{\circ}$ (sometimes at about $52-54^{\circ}$). The *hydrazide* crystallises from warm, light petroleum, in which it is readily soluble, in yellowish, hexagonal, axe-shaped plates melting at 92° with decomposition.

Acetocumeneoxime, $C_6H_4Pr^{\beta} \cdot CMe \cdot NOH$, is obtained, together with a small quantity of an oily, isomeric compound, by warming an alcoholic solution of acetocumene with hydroxylamine. It crystallises from light petroleum in rhombic plates melting at $70-71^{\circ}$. The *hydrazide* crystallises from light petroleum in long, colourless or yellowish, hexagonal plates melting at $81-82^{\circ}$.

Nitracetopropylbenzene, $[Pr^{\alpha} : NO_2 = 1 : 2]$, prepared by treating acetopropylbenzene with a mixture of concentrated sulphuric acid and fuming nitric acid, is a yellowish oil. It yields nitropropylbenzoic acid when oxidised with alkaline potassium permanganate.

Nitracetocumene, $[Pr^{\beta} : NO_2 = 1 : 2]$, crystallises in quadratic prisms or domes, melts at 49° , and is very readily soluble in benzene, but only sparingly in light petroleum. It gives metanitrocuminic acid and nitrohydroxyisopropylbenzoic acid when oxidised with alkaline permanganate.

Nitracetopropylbenzeneoxime, $NO_2 \cdot C_6H_3Pr^{\alpha} \cdot CMe \cdot NOH$, crystallises in needles or prisms, melts at 86° , and is readily soluble in benzene and sparingly soluble in light petroleum. It yields nitropropylbenzoic acid when oxidised with alkaline potassium permanganate.

Nitracetocumeneoxime, $NO_2 \cdot C_6H_3Pr^{\beta} \cdot CMe \cdot NOH$, is a colourless, crystalline compound, melts at $116-117^{\circ}$, and is readily soluble in warm benzene, but only sparingly in light petroleum.

Amidoacetopropylbenzene, prepared by reducing a dilute soda solution of nitracetopropylbenzeneoxime with ferrous sulphate, crystallises in yellow prisms, melts at $116-117^{\circ}$, and is readily soluble in alcohol and benzene, but almost insoluble in boiling light petroleum.

Amidoacetocumeneoxime, prepared in like manner, crystallises from light petroleum in prisms melting at 95° .

Nitracetopropylbenzenehydrazide, $NO_2 \cdot C_6H_3Pr^{\alpha} \cdot CMe \cdot N_2HPh$, crystallises from alcohol in slender, red needles, melts at $138-139^{\circ}$, and is sparingly soluble in boiling alcohol.

Nitracetocumenehydrazide melts at 138° .

Acetopropylbenzene is only very slowly oxidised by warm potassium permanganate, but in alkaline solution oxidation takes place extremely rapidly. Terephthalic acid is formed in both cases.

Propylbenzoic acid is best prepared by boiling 3 grams of acetopropylbenzene with 100 c.c. of nitric acid, sp. gr. 1.07, for about 10 hours. The product is distilled with steam, the distillate neutralised with potash and evaporated; the acid is then precipitated with

hydrochloric acid and crystallised from a mixture of benzene and light petroleum. F. S. K.

Benzene-derivatives of High Molecular Weight. By F. KRAFFT (*Ber.*, 21, 2265—2271).—The best source for pure palmitic acid is Japanese wax; 3 parts of the wax are saponified with a solution of 1 part of potash in 1 part of water, the acid precipitated with hydrochloric acid, and rectified once or twice in a partial vacuum. The silver salts of the higher fatty acids can be readily obtained in a pure and crystalline condition by mixing an alcoholic ammoniacal solution of the acid with a similar solution of silver nitrate; on adding water the salt separates in small plates. Pentadecyl phenyl ketone (compare F. Krafft, *Abstr.*, 1887, 252) emits light when cut or broken.

Pentadecyl paratolyl ketone, $C_{15}H_{31} \cdot CO \cdot C_6H_4Me$, prepared by gradually adding aluminium chloride to a cooled mixture of 1 part of palmitic chloride and 2 parts of toluene, and heating the mixture very slowly until it begins to boil, crystallises from alcohol in needles, melts at 60° , and boils at 262° (15 mm. pressure). It yields paratoluic acid when boiled with nitric acid, sp. gr. 1.12, for several hours, and when broken or rubbed emits bluish-green sparks of great intensity.

Heptadecyl paratolyl ketone, $C_{17}H_{35} \cdot CO \cdot C_6H_4Me$, prepared in like manner from stearic chloride and toluene, melts at 67° , boils at 278° (15 mm. pressure), and is sparingly soluble in cold alcohol, but more readily in ether and benzene. It yields paratoluic acid when oxidised with nitric acid, and emits light when cut or broken.

Pentadecyl xylyl ketone, $C_{15}H_{31} \cdot CO \cdot C_6H_3Me_2$, prepared in like manner from metaxylene and palmitic chloride, melts at 37° , boils at 268 — 269° (15 mm. pressure), and yields xylylic acid, melting at 126° , and fatty acid when boiled with nitric acid.

Pentadecyl paranisyl ketone, $C_{15}H_{31} \cdot CO \cdot C_6H_4 \cdot OMe$, obtained from palmitic chloride and anisole, melts at 70.5° , boils at 279 — 280° (15 mm. pressure), and yields anisic acid when oxidised with nitric acid. It is converted into the corresponding phenol when melted with potash and a little water.

Pentadecyl paraphenetyl ketone, $C_{15}H_{31} \cdot CO \cdot C_6H_4 \cdot OEt$, prepared from palmitic chloride and phenetole, melts at 69° , boils at 288 — 289° (15 mm. pressure), and crystallises from cold alcohol, in which it is sparingly soluble, in shining plates. It yields paraethoxybenzoic acid when oxidised with dilute nitric acid.

Pentadecyl dimethylresorcylic ketone, $C_{15}H_{31} \cdot CO \cdot C_6H_3(OMe)_2$, prepared by gradually adding aluminium chloride to a mixture of dimethylresorcinol and palmitic chloride, and heating the mixture extremely slowly from 40° to 100° , crystallises from hot alcohol in plates, melts at 63.5° , and boils at 289 — 290° (15 mm. pressure). F. S. K.

New Aromatic Diketone. By H. v. PECHMANN and H. MÜLLER (*Ber.*, 21, 2119—2120).—*Methyl phenyl diketone*, $COMe \cdot COPh$, prepared from α -nitrosopropiophenone by the action of dilute acids, forms a yellow oil heavier than water. It boils at 214° , distils with steam, and the vapour has a very penetrating odour. α -Nitroso-

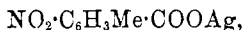
propiophene is obtained by V. Meyer's method from ethyl methylbenzoylacetate. It crystallises in white needles melting at 113° .

N. H. M.

Action of Amyl Nitrite on Nitrosoketones. By O. MANASSE (*Ber.*, 21, 2176—2177).—*Benzoylacetyl*, $\text{COPh}\cdot\text{COMe}$, is formed when nitrosoethyl phenyl ketone is heated with about $1\frac{1}{2}$ mols. of amyl nitrite. It is a yellowish oil.

F. S. K.

Nitrotoluic Acids. By S. NIEMENTOWSKI and B. ROZANSKI (*Ber.*, 21, 1992—1999).—*Orthonitroparatoluic acid*, $[\text{COOH} : \text{NO}_2 : \text{Me} = 1 : 2 : 4]$, is best prepared by heating orthonitroparatolunitrile with concentrated hydrochloric acid at about 195° . The yield is 82 per cent. It crystallises from boiling water in long, tolerably thick, yellowish needles, melts at 161° , and is almost insoluble in cold, and sparingly soluble in hot water; it is soluble in ether, benzene, and chloroform, and very readily soluble in alcohol. When heated above its melting point, it sublimes, without decomposition, in snow-white, very slender, concentrically grouped needles. The *ammonium* salt crystallises in needles or plates, which are very readily soluble in water. Lead acetate, ferric chloride, and mercuric nitrate give precipitates with a solution of the ammonium salt. The *silver* salt,



crystallises in concentrically grouped needles which are sparingly soluble in boiling water and insoluble in alcohol and cold water. The *barium* salt, $(\text{C}_6\text{H}_5\text{NO}_2)_2\text{Ba} + 4\text{H}_2\text{O}$, crystallises in nacreous leaves, and loses the whole of its water at 135° ; it is very sparingly soluble in water and rather sparingly soluble in alcohol. The *calcium* salt, $(\text{C}_6\text{H}_5\text{NO}_2)_2\text{Ca}$, crystallises in well-defined yellowish prisms, and is more sparingly soluble in water than the barium salt. The *copper* salt with 1 mol. H_2O crystallises in small, bluish-green scales, is almost insoluble in cold water and alcohol, and sparingly soluble in boiling water. All the salts of orthonitroparatoluic acid explode when heated on platinum foil.

Orthonitroparatoluyamide, obtained by heating the nitrile with an excess of potash, crystallises from boiling benzene or light petroleum in long, slender needles, melts at 153° , is readily soluble in alcohol, and soluble in water, methyl alcohol, and boiling ether. It yields orthonitroparatoluic acid when heated with concentrated hydrochloric acid. Metahomoanthranilic acid (Niemientowski, this vol., p. 837) is produced when orthonitroparatoluic acid is reduced with tin and hydrochloric acid. The yield is 46 per cent.

F. S. K.

Derivatives of Ethyl Benzoylacetate. By R. STIERLIN (*Ber.*, 21, 2120—2125).—When ethyl benzoylacetate (1 mol.) is treated with dilute potash (1 mol.) and the resulting potassium compound dissolved in much water, cooled, and an aqueous solution of diazobenzene chloride added, a brown oil separates, which is extracted with ether. The oil solidifies when kept to a half-solid mass. It crystallises from alcohol in honey-coloured, lustrous prisms, melts at 65° , is very soluble in alcohol, ether, and benzene, but not in water. The new compound

has the formula $C_{17}H_{16}O_3N_2$, and is probably a hydrazone of the constitution $NHPh \cdot N : CBz \cdot COOEt$. The *free acid*, $C_{15}H_{12}N_2O_3$, obtained by heating the ethyl salt in a water-bath with dilute potash from three to four minutes, filtering, and acidifying the well-cooled filtrate with sulphuric acid, crystallises from dilute alcohol in slender, yellow needles of a satiny lustre. It melts at 142° , dissolves very readily in alcohol, ether, and benzene, but not in water. The *salts* are bright yellow. When the ethyl salt is heated for a long time with dilute potash, the compound $COPh \cdot CH : N \cdot NHPh$ is formed. This crystallises in lustrous, yellow plates, melts at 129° , and dissolves very readily in alcohol, ether, and benzene, sparingly in hot water. The crystals have a peculiar odour.

The next homologue of the above acid is prepared from paradiazo-toluene chloride and ethyl benzoylacetate. It crystallises in slender, yellow needles of a silky lustre, and melts at $169-170^\circ$. The *ketone*, $COPh \cdot CH : N \cdot NH \cdot C_6H_4Me$, crystallises in yellowish-brown plates, melts at $122-123^\circ$, and dissolves readily in ether and benzene.

From ethyl benzoylacetate and paranitrodiazobenzene chloride the *ethyl salt*, $NO_2 \cdot C_6H_4 \cdot NH \cdot N : CBz \cdot COOEt$, was prepared. It forms very lustrous, yellow plates, melts at 114° , and dissolves readily in ether, alcohol, and benzene.

When the condensation-product from ethyl benzoylacetate and diazobenzene chloride is treated with phenylhydrazine acetate, a *pyrazole-derivative*, $\begin{smallmatrix} NPh \cdot CO \\ N : CPh - \end{smallmatrix} > C : N \cdot NHEt$, is obtained. This forms red crystals melting at 169° , readily soluble in alcohol and benzene. Warm aqueous soda dissolves it slowly with decomposition.

Ethyl benzoylacetate seems to react with phenylhydrazinesulphonic acid and sodium acetate in a similar manner. N. H. M.

Condensation of Ethyl Benzoylacetate with Succinic Acid.

By R. FITTIG and A. SCHLOESSER (*Ber.*, 21, 2133—2137).—A compound, $COOEt \cdot C \begin{smallmatrix} CPh - \\ CO \cdot CH_2 \end{smallmatrix} > CH \cdot COOH$, is formed when ethyl benzoylacetate and sodium succinate react in presence of acetic anhydride. It crystallises in short needles, melts at 112.5° , and is sparingly soluble in water.

Phenythronic acid, $C_{10}H_{10}O_5$, is obtained when the preceding compound is treated with baryta-water. It crystallises from hot water, in which it is rather easily soluble, in long, silky needles, melts at 192° , and yields a diethyl salt which is identical with that obtained from the preceding compound, and can be converted into the preceding compound by treating it carefully with alcoholic potash. When heated above its melting point, phenythronic acid yields carbonic anhydride, phenylmethylfurfuran, and a monobasic acid, *phenyvinic acid*, $C_{12}H_{10}O_3$, which crystallises in long needles, melts at $144-145^\circ$, and is insoluble in cold, and only sparingly soluble in hot water. F. S. K.

Constitution of the Compound obtained by Acting on Trimethylpyrogallol with Nitric Acid. By W. WILL (*Ber.*, 21,

2020—2026).—*Methyl gallate*, $C_6H_2(OH)_3COOMe$ [$COOMe : (OH)_3 = 1 : 3 : 4 : 5$], crystallises from ether, melts at 192° with evolution of gas, and is readily soluble in water and alcohol.

Methyl trimethylgallate, $C_6H_2(OMe)_3COOMe$, obtained by heating the preceding compound with methyl iodide, methyl alcohol, and potash, is a colourless, crystalline compound which melts at 81° and boils at 274 — 275° .

Trimethylgallic acid, $C_6H_2(OMe)_3COOH$, crystallises from ether or water in needles and melts at 167° .

Methyl pyrogallalcarboxylate, $C_6H_2(OH)_3COOMe$ [$COOMe : (OH)_3 = 1 : 2 : 3 : 4$], crystallises from water in long, shining, colourless needles which lose their water ($2\frac{1}{2}$ mols.) below 100° , and melt at 151 — 152° .

Methyl trimethylpyrogallalcarboxylate, $C_6H_2(OMe)_3COOMe$, is a colourless oil, boils at 281° , and is insoluble in water and dilute alkalis. *Trimethyl pyrogallalcarboxylic acid*, $C_6H_2(OMe)_3COOH$, separates from ether in shining crystals melting at 99° .

Propyltrimethylpyrogallol, $C_6H_2(C_3H_7)(OMe)_3$, prepared by treating propylpyrogallol with methyl iodide, methyl alcohol, and potash, is a colourless oil, boils at 164° , and is readily soluble in alcohol and ether, but insoluble in water. When warmed with concentrated nitric acid, it yields dimethoxyquinone melting at 149° (?), and when boiled with potassium permanganate it yields trimethylgallic acid.

The dimethoxyquinone formed by the action of concentrated nitric acid on trimethylpyrogallol is therefore a derivative of tetrhydroxybenzene [$(OH)_4 = 1 : 3 : 4 : 5$].

F. S. K.

Gallic Acid and Tannin. By C. BÖTTINGER (*Annalen*, **246**, 124—128).—When a solution of the purest commercial tannin is boiled with sodium acetate and phenylhydrazine hydrochloride, a yellow coloration is produced which is followed by a precipitate. This is due to the presence of a small quantity of an impurity which closely resembles tannin, and is absorbed by hide.

W. C. W.

Cocatannic Acid. By C. J. H. WARDEN (*Pharm. J. Trans.*, **18**, 985—987).—From the leaves of *Erthyroxylon coca*, grown in India, the author extracted cocatannin, $C_{17}H_{22}O_{10}$, by treatment with alcohol containing one-sixtieth of sulphuric acid. The substance, after purification, presented itself as a mass of minute filiform crystals of a yellow colour, without taste or odour, and soluble in water, alcohol, or ether. The hot aqueous solution has an acid reaction, and gives no coloration with ferrous salts, but with ferric salts a greenish coloration. The solid acid is easily soluble in alkalis, yielding yellow solutions. The aqueous solution does not precipitate gelatin. The acid appears to be bibasic, and closely allied to quercitrin.

R. R.

Hydrophthalic Acid. By A. v. BAEYER (*Ber.*, **21**, 2271—2272).—The author is investigating the hydrophthalic acids, and has found that Graebe and Born's hydrophthalic acid is a mixture of several

substances. A crystalline dihydro-acid was obtained which yields a mixture of several tetrahydro-acids when boiled with sodium amalgam and water. These acids are very readily transformed, to some extent, into isomeric compounds. Terephthalic acid also exists in forms which very readily undergo intramolecular change, so that the hydro-derivatives of benzenedicarboxylic acids exist in two kinds of mutually convertible isomeric forms, the one depending on the geometric position of the carboxyl-groups, the other on the position of the double binding.

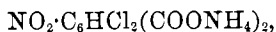
F. S. K.

Dichloroterephthalic Acid and Dichlorodihydroterephthalic Acid. By S. LEVY and A. ANDREOCCHI (*Ber.*, **21**, 1959—1964; compare this vol., p. 840).—Paradichloroterephthalic acid, purified by sublimation, melts at 305—306°.

Barium paradichloroterephthalate, $(C_6H_2Cl_2O_4)Ba + 4H_2O$, crystallises in slender needles, and is very readily soluble in water. The *silver salt*, $C_6H_2Cl_2(COOAg)_2$, is insoluble in water, and becomes rose-coloured when exposed to light.

Methyl paradichloroterephthalate, $C_6H_2Cl_2(COOMe)_2$, crystallises from methyl alcohol in colourless, nacreous plates melting at 131—132°.

Nitroparadichloroterephthalic acid, $NO_2 \cdot C_6HCl_2(COOH)_2$, is obtained in the preparation of dichloroterephthalic acid (*loc. cit.*). It crystallises from water in yellowish needles, and is readily soluble in alcohol and ether. When heated, it becomes more intensely yellow at about 180°, turns brownish-black at about 205°, and melts, with rapid evolution of gas, at 225—226°. The *ammonium salt*,



crystallises from water, in which it is very readily soluble, in orange-red needles. The *calcium salt* crystallises in orange-red needles, and is rather easily soluble in water.

Methyl nitroparadichloroterephthalate, $NO_2 \cdot C_6HCl_2(COOMe)_2$, crystallises from dilute methyl alcohol in small, colourless, shining leaves, and melts at 207—208° to a brownish-red liquid, which is decomposed on further heating.

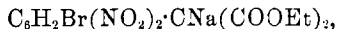
Paradichlorodihydroterephthalic acid (*loc. cit.*) is oxidised at once by alkaline permanganate, and yields dihydroterephthalic acid when treated with sodium amalgam.

F. S. K.

The Reduction-products of Terephthalic Acid. By A. v. BAEYER (*Annalen*, **245**, 138—190; see this vol., p. 1069).

Action of Ethyl Sodiomalonate on Tribromodinitrobenzene. By C. L. JACKSON and W. S. ROBINSON (*Ber.*, **21**, 2034—2035).—*Ethyl bromodinitrophenylmalonate*, $(NO_2)_2C_6H_2Br \cdot CH(COOEt)_2$, is prepared by adding an alcoholic solution of ethyl sodiomalonate to tribromodinitrobenzene dissolved in ether. After two to three hours, the whole is filtered, treated with dilute sulphuric acid, again filtered, and heated on a water-bath to get rid of the ether; on cooling, the residue

deposits crystals of the new compound. It forms flat, pale-yellow needles, melts at 75°, and dissolves readily in the usual solvents except water, in which it is insoluble. The *sodium-derivative*,



is red, and dissolves in water, alcohol, and ether.

Tribromodinitrobenzene also reacts with ethyl sodacetoacetate.

N. H. M.

Reissert's Pyranilpyroïnolactone, Pyranilpyroic and Anil-succinic Acids. By R. ANSCHÜTZ (*Annalen*, **246**, 115—123).—The anilosuccinic acid which Reissert (this vol., p. 694) obtained by the oxidation of pyranilpyroic (mesaconic) acid is in reality oxanil-acetic acid. The dihydropyranilpyroic acid and dihydropyranilpyro-lactone derived from pyranilpyroic acid are identical with the anilide and anilic acid of pyrotartaric acid.

W. C. W.

Phenoldicarboxylic Acids. By E. LIPPMANN and F. FLEISSNER (*Monatsh.*, **9**, 296—307).—When orthohydroxyquinoline (80 grams), potassium xanthate (90 grams), and sufficient absolute alcohol to form a stiff paste, are heated for 24 hours in a water-bath, the mixture becomes red, and solidifies on cooling to a hard mass from which *hydroxyquinolinecarbodithionic acid*, $\text{HO}\cdot\text{C}_6\text{H}_3\text{N}\cdot\text{CSSH}$, may be readily isolated. It forms very small red crystals which melt with decomposition at 180°, is only very sparingly soluble in water, alcohol, ether, benzene, and carbon bisulphide, but dissolves readily in alkalis, forming a red solution. The ammonium and barium salts are both only sparingly soluble in water. On oxidising the acid with alkaline permanganate, quinolinic acid melting at 231° is formed; hence the CSSH-group is attached to the benzene and not to the pyridine ring of the nucleus.

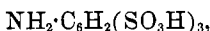
When the dithio-acid is heated with mercuric chloride, it loses sulphur and forms a new *hydroxyquinolinecarboxylic acid* crystallising in slender, lustrous needles, containing 1 mol. of water, and melting at 256° with liberation of carbonic acid and formation of orthohydroxyquinoline. The acid is more soluble in water than in alcohol, and only traces of it are dissolved by ether, benzene, and chloroform. Ferric chloride colours its aqueous solution a deep brownish-red, and ferrous sulphate in concentrated solutions precipitates the ferrous salt in the form of a brown crystalline mass. The hydrochloride crystallises in small, white needles containing $2\frac{1}{2}$ mols. of water. The potassium salt forms very pale-yellow needles, the barium, silver, and mercury salts are not characteristic, and the platinumchloride is so unstable as to be readily decomposed by water.

Resorcinolcarbodithionic acid, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CSSH}$, is obtained by heating a mixture of absolute alcohol and equivalent parts of potassium xanthate and resorcinol. It forms bright yellow needles melting at 131°, and dissolves in hot water with partial decomposition and evolution of hydrogen sulphide. It does not lose its sulphur when heated with mercuric chloride, but potash readily converts it into what seems to be a mixture of two isomeric dihydroxybenzoic

acids (resorcylic acids) which decomposes at 200°, but when heated in sealed tubes melts at 216°. Ferric chloride turns the aqueous solution red, but the colour disappears on adding excess of soda.

G. T. M.

Anilinetrisulphonic Acid. By G. T. HARTSHORN and C. L. JACKSON (*Ber.*, 21, 2032—2033).—*Anilinetrisulphonic acid*,



is prepared by heating potassium β -anilinemetadisulphonate with sulphuric acid, or aniline with an excess of sulphuric acid and the calculated amount of potassium sulphate, in a dish until the mixture begins to carbonise. It crystallises from water in flat, lustrous prisms readily soluble in hot water; when heated, it blackens and decrepitates but does not melt. The *dipotassium salt* (with 3 mols. H_2O) crystallises in thin needles; the *barium salt*, $\text{NH}_2\cdot\text{C}_6\text{H}_2\cdot\text{SO}_3\text{H}(\text{S}_2\text{O}_6\text{Ba}) + 3\frac{1}{2}\text{H}_2\text{O}$, and the *lead salt*, which forms silky needles, are described.

N. H. M.

Phenacyl Compounds. By W. STAEDL (*Ber.*, 21, 2196—2199).—Indoles can be easily obtained from phenacylanilides. When methylphenacylanilide is warmed with zinc chloride, a compound $\text{C}_{15}\text{H}_{13}\text{N}$ —probably methylphenylindole—is obtained. It crystallises in shining prisms or plates, melts at 101—102°, and is readily soluble in alcohol or benzene, but only sparingly in light petroleum. It distils without decomposition, and its alcoholic solution colours pine-wood moistened with hydrochloric acid dark red. When heated with methyl iodide and methyl alcohol, it yields a solid compound which behaves like a dihydroquinoline. The *picrate* crystallises in red needles. Methylphenacylanilide is completely decomposed when boiled with aniline for several hours with formation of methylaniline and a crystalline compound, the properties of which agree with those of 2-phenylindole.

F. S. K.

Aldine Formation. By E. BRAUN and V. MEYER (*Ber.*, 21, 1947—1949).—When esoamidoacetophenone hydrochloride is dissolved in water free from air, precipitated with ammonia free from air, and the precipitate, after keeping for some time, washed in an atmosphere of hydrogen and then without drying dissolved in hydrochloric acid, a solution of the original hydrochloride is obtained. But if the precipitate is dried in an atmosphere of hydrogen at 110°, it becomes to a great extent insoluble in hydrochloric acid, and after crystallising from boiling alcohol it yields a considerable quantity of isoindole (compare this vol., p. 700). If this same precipitate is washed in absence of air, and dried in a partial vacuum, a crystalline powder is obtained which is partly soluble in hydrochloric acid, and contains 11.9 per cent. of nitrogen.

When isonitrosomethyl ethyl ketone is reduced with stannous chloride and hydrochloric acid, a solution is obtained which does not contain tetramethylaldine (*loc. cit.*). If the solution is freed from tin by means of hydrogen sulphide, evaporated, and the residue extracted with alcoholic ether, a deliquescent salt is obtained. This salt forms a platinumchloride which is totally different from the

platinochloride of tetramethylaldine, and it yields tetramethylaldine when treated with alkali.

A base is formed when benzil monoxime is reduced with stannous chloride and hydrochloric acid; it is a colourless crystalline compound, insoluble in ether, &c., but readily soluble in dilute hydrochloric acid, and different in all respects from tetraphenylaldine. It contains 6.46 per cent. of nitrogen. A solution of its hydrochloride can be evaporated without undergoing change (*loc. cit.*). F. S. K.

Orthodinitrostilbene. By C. A. BISCHOFF (*Ber.*, **21**, 2071—2078).—*Orthodinitrostilbene*, $C_{14}H_{10}N_2O_4$, is prepared by heating a solution of 17 grams of orthonitrobenzyl chloride in 50 grams of warm 98 per cent. alcohol with a solution of 5.6 grams of potash in 56 grams of alcohol. When cold, the crystals are washed with 90 per cent. alcohol. It is then several times extracted with boiling glacial acetic acid, and the insoluble portion crystallised from chloroform, from which it separates in long, bright yellow needles melting at 196° . The acetic acid solution deposits crystals of varying melting point; in precipitating the last mother-liquor with water, and repeatedly crystallising the precipitate from glacial acetic acid, washing with alcohol and water, short, slightly grey needles are obtained which melt at 126° . Both compounds are orthodinitrostilbene; to the former (m. p. 196°), which is the chief product, the name of transorthodinitrostilbene is ascribed, and to the latter, cis-orthodinitrostilbene. This takes up bromine without evolution of hydrogen bromide, yielding a bromo-compound melting at 215° .

Transorthodinitrostilbene is insoluble in water, very sparingly soluble in alcohol, ether, and light petroleum, more soluble in benzene and carbon bisulphide; when treated with bromine, it yields the *di-bromide*, $C_{14}H_{10}N_2O_4Br_2$. This crystallises in thin, yellowish plates resembling bismuth nitrate, melts at 226° , and dissolves sparingly in hot acetone and ethyl acetate; it is more sparingly soluble than the bromine-derivative of the cis-compound.

Attempts were made to obtain a reaction between ethyl sodio-chloromalonate and orthodinitrostilbene dibromide analogous to that described by Conrad (*Abstr.*, 1881, 168) between the former compound and benzyl chloride, but without success.

Orthonitramidostilbene, $C_{14}H_{12}N_2O_2$, is obtained by heating the dinitro-compound with alcoholic ammonium sulphide for 10 hours at 100° . It is amorphous, and has no definite melting point, and is soluble in ether and alcohol. N. H. M.

Azo-dyes from Orthodiamidostilbene. By C. A. BISCHOFF (*Ber.*, **21**, 2078—2084).—*Orthodiamidostilbene*, $C_{14}H_{14}N_2$, is prepared by treating an intimate mixture of the dinitro-derivative and granulated tin with hydrochloric acid (sp. gr. 1.19), and after half an hour heating the mixture on a water-bath; the temperature rises suddenly to 110° . In 10 minutes, the reaction is complete, and on cooling the stannochloride separates. The free base crystallises in large, thin prisms of a golden lustre and melts at 176° ; the alcoholic solution shows violet-blue fluorescence. The *hydrochloride* forms concentrically

grouped needles, sparingly soluble in water; the *sulphate* crystallises in long prisms; the *platinochloride* is a yellow powder. The base is diazotised by treating 16·8 grams with 40 c.c. of hydrochloric acid (sp. gr. = 1·145), and diluting to 2 litres. 250 c.c. of this solution is diazotised at a time with the corresponding amount of nitrite.

The tetrazo-compound was treated in the usual manner with—(1) Salicylic acid; (2) Bayer's sodium naphtholsulphonate; (3) Schaeffer's sodium naphtholsulphonate; (4) α -naphthylaminesulphonic acid; (5) sodium naphtholdisulphonate (R. salt), each 2 mols. The diazo-compound was treated with the following compounds, and then further diazotised—(6) 1 mol. of α -naphthylaminesulphonic acid and 1 mol. resorcinol; (7) 1 mol. of R. salt and 1 mol. of α -naphthylaminesulphonic acid; (8) 1 mol. of R. salt and 1 mol. of phenol. The compound obtained under (4), $C_2H_2[C_6H_4 \cdot N_2 \cdot C_{10}H_5 \cdot NH_2(SO_3H)]_2$, was converted into a tetrazo-derivative, treated with 2 mols. of α -naphthylaminesulphonic acid, again tetrazotised and treated with 2 mols. of α -naphthylaminesulphonic acid; in this way, the compound $C_2H_2[C_6H_4 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot NH_2]_2$ is obtained.

Tables are given showing the properties and reactions of the dyes.

N. H. M.

Action of Heated Copper on a Mixture of the Vapours of Phenol and Carbon Bisulphide. By T. CARNELLEY and J. DUNN (*Ber.*, 21, 2005—2009).—*Diphenylene ketone*, isomeric with ordinary diphenylene ketone, is formed when phenol and carbon bisulphide are passed over heated copper, but the greater portion of the phenol is undecomposed. The ketone crystallises from alcohol in white needles or leaves, melts at 83°, is sparingly soluble in cold, more readily in hot alcohol. It is readily soluble in glacial acetic acid, insoluble in water, is not oxidised when boiled with dilute nitric acid, and is extremely stable towards oxidising agents.

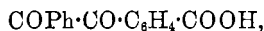
The *bromine-derivative*, $C_{13}H_7BrO$, prepared by treating a carbon bisulphide solution of the ketone with bromine, crystallises from alcohol in shining scales melting at 104°.

The *nitro-derivative*, prepared by heating the ketone with strong nitric acid at 170°, melts at 220—230°, and is insoluble in alcohol and water.

When the ketone is reduced, a compound is obtained, which crystallises from alcohol in angular plates, melts at 79—80°, and is moderately soluble in hot, but only sparingly in cold alcohol. The composition of this compound is probably $C_{45}H_{30}O_2$, or $C_{45}H_{32}O_2$.

F. S. K.

Benzilorthocarboxylic Acid. By C. GRAEBE and P. JUILLARD (*Ber.*, 21, 2003—2005).—*Benzilorthocarboxylic acid*,



is formed when desoxybenzoïn-carboxylic acid is oxidised with alkaline potassium permanganate. The reaction-product crystallises from hot water or dilute alcohol, either in dazzling white, or in pale-yellow

crystals, and sometimes both varieties occur together. The yellow colour is not due to any impurity; when the white crystals are heated at $115-125^{\circ}$, they are converted into the yellow variety. Both modifications melt at 141.5° , and are anhydrous. The white crystals are obtained when the yellow ones are dissolved in alkali and precipitated with acids.

Benzhyldroldicarboxylic acid, $\text{COOH}\cdot\text{CPh}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, is formed when benzilorthocarboxylic acid is warmed with alkalis. It is readily soluble in alcohol, benzene, and ether, sparingly soluble in water, and is converted into phenyl phthalide when heated. It has no definite melting point; when placed in a bath at $80-90^{\circ}$ it melts, and is at once decomposed. The *potassium* salt crystallises with 2 mols. H_2O .
F. S. K.

Action of Citraconic Acid on Naphthylamine. By T. MORAWSKI and M. GLÄSER (*Monatsh.*, **9**, 284—295).— *α -Naphthylamine citraconate* is formed when solutions of *α -naphthylamine* and citraconic acid dissolved in benzene are brought together in molecular proportions. It forms colourless needles, which turn yellow on exposure to light, melt at 99° , and decompose at 100° .

β -Naphthylamine citraconate is formed when alcoholic solutions of *β -naphthylamine* and citraconic acid are mixed in molecular proportions and allowed to evaporate at low temperatures. It crystallises in pale-yellow needles, which melt at $173-174^{\circ}$, with loss of water.

Citracon- α -naphthil, $\text{C}_{10}\text{H}_7\text{N}\cdot\text{C}_5\text{H}_4\text{O}_2$, is most conveniently prepared by heating together molecular proportions of citraconic acid and *α -naphthylamine* in sealed tubes at $140-150^{\circ}$ for half an hour. Crystallised from hot alcohol, it forms beautiful yellow plates, which melt at $142-143^{\circ}$, and boil at 360° with partial decomposition. The corresponding *β -naphthylamine* compound is prepared in a similar way, and much resembles its isomeride. It crystallises from most of the ordinary solvents in very small needles.

On brominating 1 mol. of the *α -compound* dissolved in acetic acid with 2 mols. of bromine, the dibromo-derivative, $\alpha\text{-C}_{10}\text{H}_6\text{Br}\cdot\text{N}\cdot\text{C}_5\text{H}_3\text{BrO}_2$, is formed; this crystallises in pale-yellow prisms, and melts at 199° . The corresponding dibromo- *β -derivative* forms yellow needles melting at 181° .
G. T. M.

Action of Ammonium Sulphide on some Dinitro-compounds. By E. HEIM (*Ber.*, **21**, 2301—2309).—*Dinitrophenyl- α -naphthylamine* is obtained by heating bromodinitrobenzene (1 mol.) with *α -naphthylamine* (1 mol.) in alcoholic solution (compare Heim, this vol., p. 488). It crystallises from glacial acetic acid or absolute alcohol in orange-red needles, melts at 190.5° , is very readily soluble in benzene, toluene, acetone, and chloroform, but insoluble in water. It dissolves in alcoholic potash, yielding a dark-red, and in concentrated sulphuric acid, forming a dark-blue solution.

Nitroamidophenyl- α -naphthylamine, prepared by reducing the preceding compound with ammonium sulphide in alcoholic solution, crystallises from alcohol or acetic acid in dark-yellow needles, melts at $145-147^{\circ}$, and is very readily soluble in alcohol, glacial acetic acid,

chloroform, warm benzene, and toluene, moderately soluble in ether, and sparingly in hot water. It dissolves in concentrated sulphuric acid, forming a dark blue solution, from which water precipitates brown flocks. The amido-group is in the ortho-position to the imido-group.

Nitrazoimidophenyl- α -naphthylamine, $C_{10}H_7 \cdot N < \overset{C_6H_3(NO_2)}{N \equiv N} >$, is obtained by treating an alcoholic solution of the preceding compound with hydrochloric acid and ethyl nitrite. It crystallises from hot absolute alcohol, in which it is only sparingly soluble, in cinnamon-brown, shining needles, melts at 182° , is readily soluble in acetone and chloroform, moderately soluble in benzene, toluene, and hot glacial acetic acid, sparingly in ether and carbon bisulphide, and insoluble in water. It dissolves in concentrated sulphuric acid, forming a dark-green solution, from which it is precipitated unchanged by water, as is also the case with the solution in hot alcoholic potash.

Nitrophenophenanthrazine, $C_{20}H_{11}N_3O_2$, is obtained by heating nitrophenyleneorthodiamine with a glacial acetic acid solution of phenanthraquinone. It melts at 251° , and at a higher temperature sublimes in slender, yellow needles, with only slight decomposition. It is insoluble in water, very sparingly soluble in alcohol, ether, and glacial acetic acid, moderately soluble in acetone, and readily in chloroform, and boiling benzene or toluene. It gives a purple-red solution with concentrated sulphuric acid, but on adding water the colour changes to orange, and finally yellow flocks are precipitated.

Amidophenophenanthrazine, melting at 179° , is identical with the compound obtained by Witt (Trans., 1886, 401) from phenanthraquinone and a solution of reduced chrysoidine.

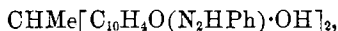
Nitroethenylorthophenylenediamine, $C_6H_3(NO_2) < \overset{N}{\underset{NH}{\parallel}} > CMe$, is obtained when nitro-orthophenylenediamine is heated for four hours at 190° with acetic anhydride. It crystallises in yellowish-brown, well-defined needles containing water, which is given off at 120° . It melts at 216° , is readily soluble in alcohol, benzene, chloroform, acids, and hot water, and moderately soluble in ether.

Nitroamidodimethylaniline, $C_6H_{11}N_3O_2$, prepared by reducing dinitrodimethylaniline with alcoholic ammonium sulphide, crystallises from boiling water in orange-yellow needles, melts at 63° , and is sparingly soluble in hot water, but readily soluble in ordinary organic solvents, and in dilute mineral acids. It distils in small quantities with steam or alcohol vapour, but soon decomposes in aqueous or alcoholic solution. It is not changed by heating with alcoholic potash, and yields a crystalline *acetyl*-derivative. Paranitrodimethylaniline is obtained when an alcoholic solution of the preceding compound is treated with hydrochloric acid and ethyl nitrite. F. S. K.

Phenylhydrazine-derivatives of Hydroxynaphthaquinone. By T. ZINCKE and H. THELEN (*Ber.*, 21, 2200—2205).—*Benzaldehydihydroxynaphthaquinone*, $CHPh(C_{10}H_4O_2 \cdot OH)_2 [OH : CHPh = 2 : 3]$, is readily obtained by heating 1 part of hydroxynaphthaquinone with 1 part of benzaldehyde and 2—3 parts of alcohol at 100° for some

hours. It crystallises from dilute acetic acid, or from a mixture of benzene and light petroleum in small, bright-yellow needles, melts at 211—214°, and is readily soluble in alcohol, glacial acetic acid, ether, chloroform, and benzene, but almost insoluble in light petroleum. When warmed with phenylhydrazine in alcoholic solution, it yields the same compound ($C_{39}H_{28}N_4O_4$) as is obtained from hydroxynaphthaquinone hydrazide and benzaldehyde (Abstr., 1884, 1359).

Ethylidenedishydroxynaphthaquinonehydrazide,



prepared by heating an alcoholic solution of hydroxynaphthaquinonehydrazide with acetaldehyde, crystallises from chloroform or aniline in small, dark-red needles, melts at 258° with decomposition, and is sparingly soluble in hot benzene or hot acetic acid, but almost insoluble in alcohol.

Acetone and hydroxynaphthaquinonehydrazide yield a condensation product, which crystallises from chloroform in reddish-yellow needles; it melts at 245—250°, and is readily soluble in alcoholic, but insoluble in aqueous alkali.

F. S. K.

Terpenes. By O. WALLACH (*Annalen*, **245**, 241—278; compare this vol., p. 60).—*Pinene nitrosochloride*, $C_{10}H_{16}NOCl$, is prepared by mixing 14 c.c. of pinene, 20 c.c. of amyl nitrite, and 34 c.c. of glacial acetic acid; to each 6 c.c. of this mixture, which is well cooled, 3 c.c. of a mixture of equal volumes of hydrochloric (33 per cent.) and acetic acids is gradually added, so that the blue colour produced disappears each time before the addition of fresh acid. The *nitrosobromide*, $C_{10}H_{16}NOBr$, is obtained by very gradually adding 7 c.c. of 60 per cent. hydrobromic acid diluted with 10 c.c. of alcohol to a well-cooled mixture of 14 c.c. of oil of turpentine, 20 c.c. of amyl nitrite, and 20 c.c. of alcohol. It melts at 91—92°, and resembles the nitrosochloride. *Pinene nitrol-piperidine*, $C_{10}H_{16}NO\cdot C_5NH_{10}$, prepared by heating the nitrosochloride with an excess of pure piperidine, melts at 118—119°; the *hydrochloride* is sparingly soluble. Camphene could not be made to combine with nitrosyl chloride.

Limonene nitrosochloride is also readily prepared by the method given for the pinene-derivative; the *hydrochloride*, $C_{10}H_{16}NOCl\cdot HCl$, melts at 113—114°. *Limonene nitrosobromide*, $C_{10}H_{16}NOBr$, melts at 90.5°. *Limonene nitrosate*, $C_{10}H_{16}NO(ONO_2)$, is formed when a mixture of equal volumes of limonene and amyl nitrite is cooled and treated with $\frac{1}{2}$ vol. of glacial acetic, 1 mol. of nitric acid (sp. gr. = 1.395); it was not purified or analysed. *Limonene hydrochloride*, $C_{10}H_{17}Cl$, is prepared by adding 100 c.c. of limonene to a mixture of 100 c.c. of fuming hydrochloric acid (38 per cent.) and 100 c.c. of glacial acetic acid, heating the whole for some hours at 70°, pouring it into water, and distilling in a vacuum. It is dextrorotatory. Sp. gr. = 0.98°. Mol. refraction = 49.86. It boils at 90° in a vacuum, but when kept the boiling point is much higher. *Hydrochloro-limonene nitrosate*, $C_{10}H_{17}ClNO(ONO_2)$, is obtained by the action of 60 per cent. nitric acid on a mixture of limonene chloride and amyl nitrite; it is identical with the compound obtained by Maissen from

limonene (*loc. cit.*). The *nitrosochloride*, $C_{10}H_{17}Cl.NOCl$, prepared from the chloride in a manner similar to the nitrosochloride from limonene, melts at 109° . *Hydrochlorolimonene nitrolanilide*,



is formed when 13 grams of the nitrosate, $C_{10}H_{17}Cl.N_2O_4$, is treated with 9 grams of aniline and 40 c.c. of alcohol; it melts at 135 – 136° . *Hydrochlorolimonene nitrolparatoluidide*, $C_{10}H_{17}Cl.NO \cdot NH \cdot C_6H_4Me$, prepared like the anilide, crystallises with 1 mol. EtOH in well-formed octahedra, melting at 135° ; when free from alcohol, it melts at 145 – 146° . When a mixture of 13 grams of the hydrochloronitrosate, 6 grams of dimethylaniline, and 50 c.c. of alcohol is heated, the compound $C_{10}H_{17}Cl.NO \cdot OEt$ is formed. It separates from its alcoholic solution in well-formed crystals melting at 144 – 145° . If methyl alcohol is used instead of ethyl alcohol, the compound $C_{10}H_{17}Cl.NO \cdot OMe$, crystallising in well-formed prisms melting at 139° is obtained. All the derivatives obtained from the hydrochloronitrosate yield non-chlorinated compounds when boiled with alcoholic potash.

Dipentene dichloride is readily prepared by passing hydrogen chloride over (not into) dipentene diluted with $\frac{1}{2}$ vol. of glacial acetic acid. The *nitrosochloride*, $C_{10}H_{18}.NOCl$, is obtained by shaking a well-cooled mixture of 6 c.c. of pure dipentene, 6 c.c. of methyl alcohol, and 9 c.c. of amyl nitrite with 7 c.c. of fuming hydrochloric acid, which is gradually added. It melts at 101 – 102° , and is optically inactive. It is converted by alcoholic potash into the compound $C_{10}H_{18}NO$ (isomeric with carvoxime), which melts at 92 – 93° , dissolves very sparingly in boiling water, more readily in hot alcohol, and is optically active. Goldschmidt and Kisser obtained (*Abstr.*, 1887, 925) by the action of dilute sulphuric acid on isocarvoxime a compound of the formula $C_{10}H_{18}NO$, melting at 94° . *Dipentene nitrolpiperidine*, $C_{10}H_{18}.NO \cdot C_5NH_{10}$, crystallises from alcohol in colourless needles melting at 153 – 154° . The *nitrosate*, $C_{10}H_{18}.NO(ONO_2)$, is prepared by adding 3.5 grams of nitric acid (sp. gr. = 1.395) to 5 grams of dipentene, 4 grams of amyl nitrite, and 2 c.c. of glacial acetic acid previously cooled. Alcohol is added until a clear solution is formed, and then water until just turbid. It is then left for some hours in a freezing mixture. It crystallises in lozenge-shaped plates, melts at 84° with decomposition, and dissolves very readily in benzene. When heated with alcoholic potash, the nitroso-compound melting at 93° is formed. The *hydrochloride*, $C_{10}H_{18}.N_2O_4.HCl$, was prepared.

Sylvestrene nitrosochloride, $C_{10}H_{18}.NOCl$, melts at 106 – 107° , and dissolves very readily in chloroform. It is strongly dextrorotatory.

Terpinene benzoylisonitrosite, $C_{10}H_{18}(ONO).NO \cdot C_6O_2H$, is prepared by adding 20 grams of benzoic chloride to 30 grams of terpinene nitrosite, and 300 c.c. of dry ether, and keeping the whole in a closed vessel for some days. It crystallises from alcohol in plates melting at 77 – 78° . It is probable that terpinene nitrosite is a nitroso-compound, $NO \cdot C_{10}H_{18} \cdot ONO$, and that in presence of reagents it has a tendency to go over into an isonitroso-compound. N. H. M.

Cheken Leaves. By F. WEISS (*Pharm. J. Trans.*, **18**, 1051—1053).—The most important constituent of cheken leaves (*Myrtus cheken*) is an ethereal oil of greenish-yellow colour and pleasant odour, which on slow evaporation leaves 5 per cent. of a resinous matter. The oil is not changed by cold, and is miscible with ether, chloroform, and absolute alcohol in all proportions. Its specific gravity is 0.8975 at 15°, and polarisation $[\alpha]_D^{20} = +23.5^\circ$. Its chief constituent is a fluorescent hydrocarbon, $C_{10}H_{16}$; boiling point, 156° (uncorr.); sp. gr. = 0.8635 at 15°; rotatory polarisation, $[\alpha]_D^{20} = 31.28^\circ$, identical with Wallach's pinene. A second portion containing oxygen yields with bromine brick-red crystals of cineol dibromide (Wallach), and is therefore cineol. The third portion is a dense yellow oil, smelling strongly of cheken. From the leaves, after separation of the ethereal oil, the author obtained by extraction with alcohol, &c., several principles, which, after isolation by processes described in the paper, he examined, and has described as *chekenone*, $C_{40}H_{64}O_8$, an indifferent substance, melting at 203—204°, and resisting ordinary reagents; *chekenic acid*, $C_{12}H_{11}O_3$, melting at 224—225°, and forming yellow, easily decomposed compounds with bases; *cheken bitter*, an intensely bitter substance, with unpleasant odour, but without toxic properties; *chekenetin*, yellow-green, acicular crystals, $C_{11}H_7O_6 + H_2O$, which form bright green-coloured solutions with alkalis, changing to blue-violet, and finally to onion-peel red. This colouring principle is, the author believes, allied to the quercetin-group. R. R.

Apiole. By G. CIAMICIAN and P. SILBER (*Ber.*, **21**, 2129—2133).—Apiolaldehyde (compare this vol., p. 847) is best obtained from isapiole by treating the latter, in a glacial acetic acid solution, with chromic acid, the yield being 35 to 40 per cent.

Acetyl apiolaldoxime, $C_9H_9O_4(CH:N\cdot O\cdot COMe)$ (*loc. cit.*), crystallises from alcohol in long, shining prisms, melts at 128—129°; it is soluble in hot alcohol and ether, but only sparingly soluble in hot, and almost insoluble in cold, water. It gives the same colour reaction with sulphuric acid as apiolaldoxime (*loc. cit.*).

Bibromopione, $C_9H_8Br_2O_4$, prepared by warming a glacial acetic acid solution of apiolic acid or apiolaldehyde with an excess of bromine, crystallises from alcohol in prisms or needles, melts at 99—100°, and gives the sulphuric acid reaction. It is readily soluble in ether, ethyl acetate, warm alcohol, and glacial acetic acid, but sparingly soluble in warm, and almost insoluble in cold water.

From its behaviour when heated with hydriodic acid, apiolic acid probably contains two methoxy-groups.

A nitro-compound, probably $C_8H_8N_2O_7$, is formed when apiolic acid is nitrated; it crystallises in long, flat, yellow needles, melts at 118°, and is soluble in ether, alcohol, and acetic acid, but insoluble in water and aqueous alkalis. F. S. K.

Cubebin. By C. POMERANZ (*Monatsh.*, **9**, 323—326; compare this vol., p. 162).—When cubebin is oxidised with permanganate in alkaline solution, it yields piperonylic acid, and may therefore be regarded as a compound derived from the group $CH_2O_4:C_6H_4$, in which one of

the atoms of hydrogen in the benzene nucleus is replaced by the group C_4H_5O . By the action of benzoic chloride on cubebin, hydrogen chloride is liberated, and an atom of hydrogen in the C_3H_5O -group is displaced by benzoyl, hence the oxygen is present in the form of hydroxyl. From the benzoyl-derivative, benzoic acid may be readily regenerated by hydrolysis. Cubebin, therefore, has the constitution $H_2C:O_2:C_6H_3:C_3H_4:OH$ [$O_2 : C_3H_5O = 1 : 2 : 4$]. G. T. M.

Organic Compound which Hydrogenises Sulphur in the Cold. By J. DE REY-PAILHADE (*Compt. rend.*, **106**, 1683—1684).—Dried yeast suspended in its own volume of alcohol of 86° , and agitated frequently for two days in a closed flask, yields a limpid yellowish liquid with an acid reaction. If sulphur, moistened with alcohol, is introduced into this solution, hydrogen sulphide is evolved. When yeast, triturated with sulphur, is introduced into a solution of sugar, carbonic anhydride and hydrogen sulphide are evolved, as Dumas previously observed.

The action of this substance is greater at 35 — 40° than at the ordinary temperature, but if the alcoholic solution is heated to 70° and cooled, it becomes turbid and loses its power of producing hydrogen sulphide. The same change takes place slowly at the ordinary temperature. The power of hydrogenising sulphur also gradually disappears if fresh yeast is suspended in solutions of acids or alkalis, or is triturated with neutral salts. Water or ether, agitated with fresh yeast, acquires no such power.

Fresh animal tissues, macerated with their own weight of alcohol of 86° , yield a solution which gives no hydrogen sulphide with sulphur. If, however, the residue is triturated with sulphur, hydrogen sulphur is given off in considerable quantity. It follows that the substance, to which the author gives the name *philothion*, exists in animal tissues in a form different from that in which it exists in yeast. It stands to sulphur in the same physiological relation as hæmoglobin to oxygen, that is to say, it renders it soluble and assimilable.

C. H. B.

Philothion. By J. DE REY-PAILHADE (*Compt. rend.*, **107**, 43—44).—Philothion (preceding Abstract) is formed in the life processes of yeast, and when the latter is treated with various reagents, its death always precedes the destruction of the philothion. Concentrated methyl alcohol readily extracts it from yeast. A current of air passed through an alcoholic solution for two hours causes no appreciable decomposition of philothion.

Philothion exists in white of egg and in fresh sheep's blood, but not in lamb's bile or human urine. It occurs to some extent in plants, and is found, for example, in the tips of young shoots of asparagus. It does not exist, however, in the young seeds of beans and peas.

C. H. B.

Oxyazoles and their Derivatives. By M. LEWY (*Ber.*, **21** 2192—2196 (compare this vol., p. 55)).—*Phenylmethyloxyazole*,



is formed when chloracetone is heated with 2 mols. of benzamide for about two hours. It is a colourless oil, boils at 238—241°, turns yellow on exposure to the air, and is soluble in strong acids. The *platinochloride*, $(C_{10}H_9NO)_2, H_2PtCl_6 + 2H_2O$, crystallises from dilute hydrochloric acid in bright yellow, slender needles, melting at 170°.

Methylphenylimidazole, $\begin{matrix} N:CPh \\ | \\ CH:CM_e \end{matrix} > NH$, is obtained by heating the preceding compound with an excess of concentrated alcoholic ammonia at 220—230°. It crystallises from aqueous alcohol in long, white needles, melts at 158—159°, and is very readily soluble in strong alcohol or benzene, but only sparingly in ether and cold water. It distils slowly with steam, and when heated alone distils with partial decomposition. The *hydrochloride*, $C_{10}H_{10}N_2, HCl$, crystallises from hot water in long, slender, white needles, which melt at 242° with decomposition. The *platinochloride*, $(C_{10}H_{10}N_2)_2, H_2PtCl_6 + 2H_2O$, crystallises from hot water in large, yellow, flat prisms, melting at 210—212° with decomposition. F. S. K.

Hydantoïns. By A. PINNER (*Ber.*, 21, 2320—2329).—The metapyrazolone-derivatives described by Pinner and Lifschütz (*Abstr.*, 1887, 1054), must be regarded as derivatives of hydantoin.

α-Phenylhydantoin (phenylmetapyrazolone), $\begin{matrix} CHPh \cdot CO \\ | \\ NH \cdot CO - \end{matrix} > NH$, separates in long, white needles, melting at 178°, when 145 grams of benzaldehydecyanhydrin are heated at 100° with 60 grams of carbamide, the product washed with ether, and the residual nitrile warmed with dilute hydrochloric acid for 15 minutes. If, however, the nitrile is heated with concentrated hydrochloric acid for several hours the phenylhydantoin separates in plates, melting at 178°. Both kinds of crystals retain their specific form when recrystallised from water.

The salt, $C_9H_7KN_2O_2$, separates in small, white needles when the crystalline plates are dissolved in concentrated alcoholic potash (1 mol.) and the solution kept. It is sparingly soluble in alcohol, but readily soluble in water, and the crystalline plates melting at 178° are again obtained when a concentrated aqueous solution is precipitated with hydrochloric acid. It is converted into the potassium salt of pseudophenylhydantoin when recrystallised from alcohol.

The *potassium* salt of pseudophenylhydantoin, $C_9H_7N_2O_2K$, separates in slender, white needles, when phenylhydantoin is boiled with an alcoholic solution of potash (2 mols.); it is almost insoluble in water.

Pseudophenylhydantoin, $\begin{matrix} CHPh \cdot CO \\ | \\ O \cdot C(NH) \end{matrix} > NH$, is obtained by treating an aqueous solution of the potassium salt with hydrochloric or acetic acid. It is crystalline, insoluble in water and alcohol, and decomposes when heated above 300°, but does not melt.

The conversion of phenylhydantoin into the pseudo-form does not take place in aqueous, but only in alcoholic solution, and is best carried out very slowly, and at the ordinary temperature, as a little

phenylamidoacetic acid is formed when the solution is heated. Phenylhydantoïn is also partially converted in the pseudo-form when hydrogen chloride is passed into an alcoholic solution for a long time.

Methylphenylhydantoïn, $\langle \begin{smallmatrix} \text{CHPh}\cdot\text{CO} \\ \text{NH}\cdot\text{CO}- \end{smallmatrix} \rangle \text{NMe}$, is obtained by heating an absolute methyl alcoholic solution of phenylhydantoïn with potash (1 mol.) and methyl iodide. It crystallises from alcohol in long needles, melts at $161-162^\circ$, is sparingly soluble in cold alcohol and dilute alkalis, but readily in hot alcohol.

Ethylphenylhydantoïn, prepared in like manner, separates from water in an oily condition, but soon solidifies to compact, shining prisms melting at 94° . It is readily soluble in alcohol, ether, benzene, and dilute alkalis, moderately soluble in hot, but only sparingly in cold water. It yields barium carbonate, ethylamine, and phenylamidoacetic acid, when heated with an excess of baryta-water, thus proving the constitution assigned to phenylhydantoïn.

Ethylpseudophenylhydantoïn, $\langle \begin{smallmatrix} \text{CHPh}\cdot\text{CO} \\ \text{O}\cdot\text{C}(\text{NH}) \end{smallmatrix} \rangle \text{NEt}$, separates when a dilute alkaline solution of ethylphenylhydantoïn is kept for some time. It is also obtained by heating a dilute alcoholic solution of pseudophenylhydantoïn with potash (1 mol.) and ethyl bromide. It crystallises in white needles, is sparingly soluble in alcohol, ether, benzene, and boiling amyl alcohol, and insoluble in water. When heated above 300° , it decomposes, but does not melt, and it yields equal quantities of ammonia and ethylamine, together with phenylhydroxyacetic acid, when heated with an excess of baryta-water. This reaction shows that pseudophenylhydantoïn has the constitution given above.

α -Phenylhydantoïc acid, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{COOH}$, is obtained when phenylhydantoïn is boiled with baryta-water until the solution commences to become turbid. It crystallises from water in colourless prisms, is sparingly soluble in cold, but readily in hot water, and melts at 178° with evolution of carbonic anhydride and ammonia. When pseudophenylhydantoïn is heated with baryta-water until the solution is distinctly turbid, it yields small quantities of ammonia, carbonic anhydride, and phenylhydroxyacetic acid, but the greater portion remains unchanged.

The *acetyl*-derivative of phenylhydantoïn crystallises from benzene in small needles, melts at 145° , is readily soluble in alcohol, moderately soluble in benzene, sparingly in ether, and insoluble in water. It is readily saponified by soda.

F. S. K.

Higher Homologues of the Synthetical Pyridines and Piperidines. By A. JACCKLE (*Annalen*, **246**, 32—52).—The ethylic salt of normal propylitidinehydrodicarboxylic acid,



is obtained by adding normal butaldehyde (1 mol.) to a mixture of alcohol and ethyl acetoacetate (2 mols.), in which ammonia (1 mol.) is dissolved. The ethereal salt melts at 118° , crystallises in prisms, and dissolves freely in alcohol and ether. The alcoholic solution

yields *ethyl normal propyllutidinedicarboxylate*, $C_5NMe_2Pr^a(COOEt)_2$, on oxidation with nitrous acid. This substance is an oily liquid, boiling at 308° . The *platinochloride*, $(C_{16}H_{23}NO_4)_2 \cdot H_2PtCl_6$, forms orange-coloured prisms and melts at 187° . The free acid,



is freely soluble in hot water and melts at 211 – 212° . The anhydrous acid melts at 247° . When heated with lime, it yields normal *propyllutidine*, $C_5NH_2Me_2Pr$, boiling at 193 – 196° under a pressure of 718 mm. The hydrochloride and platinochloride are crystalline.

Ethyl hexyllutidinehydrodicarboxylate, prepared by the action of ammonia on ethyl acetoacetate and cœnanthol, crystallises in prisms of a yellow colour, and melts at 54° . *Ethyl hexyllutidinedicarboxylate*, $C_6H_{13} \cdot C_5NMe_2(COOEt)_2$, is an oil which crystallises with difficulty. The *platinochloride* forms orange-coloured plates and melts at 141° . The free acid was not obtained in the pure state. *Normal hexyllutidine*, $C_6H_{13} \cdot C_5NH_2Me_2$, boils at 249 – 251° . The hydrochloride is deliquescent, but the platinochloride crystallises in beautiful prisms melting at 163° . The alcoholic solution of the base gives, with silver nitrate, a precipitate of the composition $(C_{13}H_{21}N)_2AgNO_3$. Symmetrical piperidines were prepared by the action of sodium on the alcoholic solutions of the corresponding pyridines by Ladenburg's process (Abstr., 1884, 1202). Symmetrical *trimethylpiperidine* or *copellidine*, $C_5NH_5Me_3$ [$Me_3 = 2 : 4 : 6$], boils between 145° and 147° . It is freely miscible with alcohol and ether, and forms crystalline salts, most of which dissolve freely in water. The platinochloride crystallises in orange plates and melts at 205° . Symmetrical *parpevoline* or *ethyl lupetidine*, C_6NH_5MeEt [$Me_2 : Et = 2 : 6 : 4$], boils at 165 – 167° under 725 mm. pressure. The *platinochloride*, $(C_9H_{13}N)_2 \cdot H_2PtCl_6$, and the *dichromate*, $(C_9H_{13}N)_2 \cdot H_2Cr_2O_7$, crystallise in prisms. Symmetrical *propyllupetidine*, $C_5NH_5Me_2Pr^a$, boils at 178 – 183° under 718.4 mm. pressure. The crystalline platinochloride melts at 197° . Symmetrical *isobutyllupetidine*, $C_5NH_5Me_2 \cdot CH_2 \cdot CHMe_2$, boils at 196 – 198° under a pressure of 720 mm. The hydrochloride and hydrobromide are crystalline, but the dichromate and platinochloride are not. Symmetrical *hexyllupetidine*, $C_5NH_5Me_2 \cdot C_6H_{13}$, boils at 239 – 242° under 715 mm. pressure. The hydrochloride is crystalline.

The poisonous character of these piperidines increases with the molecular weight.

The minimal fatal dose for a frog is 0.02 gram of lupetidine, 0.01 gram of copellidine, 0.05 gram of parpevoline, or 0.004 gram of hexyllupetidine. In the case of poisoning with the piperidines, the red blood corpuscles are perforated, but the number and size of the holes diminishes as the molecular weight of the base increases.

W. C. W.

Conversion of Piperidine into δ -Amidovaleric Acid and into Oxypiperidine. By C. SCHOTTEN (*Ber.*, 21, 2235–2254).—Benzoyl- δ -valeric acid is identical with benzoylhomopiperidinic acid (Abstr., 1885, 176), and can be obtained by acting on a mixture of 1 mol. of δ -amidovaleric acid and 1 mol. of benzoic chloride with an aqueous solution of 1 mol. of soda. The acid is decomposed into

benzoic acid and piperidine when distilled. The *barium* salt is anhydrous and readily soluble.

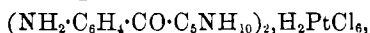
Benzoyl- δ -amidovaleric anhydride, $\text{COPh}\cdot\text{C}_6\text{H}_5\text{NH}_2\text{O}$, obtained by boiling the acid with acetic anhydride, crystallises from alcohol in nacreous plates, melts at 112° , is sparingly soluble in ether, and insoluble in soda or sodium carbonate.

δ -Amidovaleric acid, $\text{NH}_2\cdot\text{C}_6\text{H}_5\cdot\text{COOH}$ (normal), prepared by heating the benzoyl-derivative with hydrochloric acid, crystallises in colourless, nacreous plates, is extremely soluble in water, less readily in dilute alcohol, almost insoluble in absolute alcohol, and insoluble in ether. It melts and decomposes at 157 – 158° , yielding water and oxypiperidine, and when heated with alkalis yields carbonic anhydride and butylamine. It forms salts both with acids and with bases, all of which are readily soluble in water. The *hydrochloride* crystallises in prisms. The *barium* salt is crystalline, and is not decomposed by carbonic anhydride.

Oxypiperidine, $\text{C}_6\text{H}_9\text{ON}$, formed as stated above, is a colourless, crystalline compound, melts at 39 – 40° , boils at 256° , and is extremely soluble in water, alcohol, ether, and dilute acids, but insoluble in concentrated potash or soda. It is precipitated from neutral or acid aqueous solutions by the usual reagents for alkaloids, and when boiled with concentrated acids or alkalis is reconverted into δ -amidovaleric acid. Oxypiperidine is a tolerably strong poison, its action being very similar to that of strychnine. The *acetyl*-derivative, $\text{C}_6\text{H}_9\text{ONAc}$, is a colourless liquid, boils at 238° , and is readily soluble in water, alcohol, and ether.

Metanitrobenzoylpiperidine, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_9\text{N}$, is obtained by mixing 1 mol. of metanitrobenzoic chloride and 1 mol. of piperidine with a concentrated aqueous solution of 1 mol. of potash or soda. It crystallises from alcohol in dark yellow, pyramidal prisms, melts at 83 – 84° , and is readily soluble in alcohol and ethyl acetate, but rather sparingly in ether. It crystallises from hot water, in which it is only very sparingly soluble, in plates containing water (as much as 29.1 per cent.), the quantity of which seems to vary with the concentration and temperature of the solution; the crystals lose their water on exposure to the air. It dissolves in concentrated hydrochloric or fuming nitric acid, and is reprecipitated unchanged by water; when boiled with concentrated nitric acid, it is only attacked very slightly, a small quantity of butyric or valeric acid being formed. It yields small quantities of pyridine or bromopyridine when boiled with a glacial acetic acid solution of bromine.

Amidobenzoylpiperidine, prepared by reducing the preceding compound with ammonium sulphide, separates from hot water in long, colourless crystals, melts at 125° , and is soluble in alcohol, but almost insoluble in water. The *platinochloride*,



crystallises in shining needles, and is almost insoluble in water.

Metanitrobenzoyl- δ -amidovaleric acid, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_9\text{O}_2$, obtained by oxidising metanitrobenzoylpiperidine with potassium permanganate, crystallises from water in small, colourless, rhombic

tables, from alcohol in yellowish, shining plates, and from ethyl acetate in colourless prisms melting at 134—135°. It is almost insoluble in very dilute hydrochloric acid and in ether, rather easily in alcohol, but less readily in cold ethyl acetate. The *barium* salt, $(C_{12}H_{13}N_2O_5)_2Ba + 2\frac{1}{2}H_2O$, crystallises from water in rhombic and in hexagonal plates, which are readily soluble in water, but sparingly soluble in alcohol. The *cadmium* salt, $(C_{12}H_{13}N_2O_5)_2Cd + 7H_2O$, and the *zinc* salt are crystalline, but the *silver* salt is amorphous. The acid yields metanitrobenzoic acid and δ -amidovaleric acid when boiled with concentrated hydrochloric acid. The *anhydride*, $NO_2 \cdot C_6H_4 \cdot CO \cdot N \cdot C_5H_9O$, obtained by boiling the acid with acetic anhydride, crystallises from dilute alcohol in shining, yellowish plates melting at 114°.

Parabromobenzoic chloride crystallises in long, colourless prisms, melts at 42°, and boils at 174° (102 mm. pressure.)

Parabromobenzamide crystallises from hot water in colourless needles, melts at 190°, and is rather easily soluble in alcohol, but sparingly soluble in ether.

Parabromobenzoylpiperidine, $C_8H_8Br \cdot CO \cdot C_5NH_{10}$, prepared from parabromobenzoic chloride and piperidine, crystallises from alcohol in large, clouded, rectangular plates, melts at 95°, and is readily soluble in alcohol, but only sparingly in ether or water.

Parabromobenzoyl- δ -amidovaleric acid, $C_6H_4Br \cdot CO \cdot NH \cdot C_5H_9O_2$, prepared by oxidising the preceding compound with potassium permanganate, crystallises from 90 per cent. hot alcohol in needles, melts at 180—181°, and is sparingly soluble in water and ether. It yields a crystalline anhydride when boiled with acetic anhydride. The alkaline salts are readily soluble in water. The *barium* salt, $(C_{12}H_{13}BrNO_3)_2Ba$, crystallises from hot water, in which it is readily soluble, in nacreous plates.

Orthobromobenzoic chloride is a colourless liquid boiling at 158° (49 mm. pressure). *Orthobromobenzamide* crystallises from hot water in needles, melts at 155—156°, and is sparingly soluble in ether.

Orthobromobenzoylpiperidine is a thick, yellowish oil, and behaves towards solvents like the corresponding para-compound.

Orthobromobenzoyl- δ -amidovaleric acid, obtained by oxidising the preceding compound with potassium permanganate, is a crystalline compound which melts at 110—111°, and is readily soluble in alcohol, but only sparingly in ether or water. It yields a crystalline anhydride when boiled with acetic anhydride. The alkaline salts and those of the alkaline earths are readily soluble in water, but those of the heavy metals only sparingly. The *silver* salt, $C_{12}H_{13}BrNO_3Ag$, is crystalline.

Salicylpiperidine, $OH \cdot C_6H_4 \cdot CO \cdot C_5NH_{10}$, is formed when methyl salicylate is heated with anhydrous piperidine. It crystallises from alcohol in thin, yellowish plates, melts at 142°, is sparingly soluble in ether, and almost insoluble in cold water and dilute acids, but readily soluble in hot soda.

Parahydroxybenzoylpiperidine, $OH \cdot C_6H_4 \cdot CO \cdot C_5NH_{10}$, is obtained when piperidine parahydroxybenzoate is treated with phosphorus chloride in the cold. It crystallises from dilute alcohol in thick

prisms, melts at 210° , and behaves towards solvents like salicyl-piperidine.
F. S. K.

Tertiary Phenylpiperidine. By E. LELLMANN and W. GELLER (*Ber.*, **21**, 2279—2281 (compare Lellmann, *Abstr.*, 1887, 604, and Lellmann and Geller, this vol., p. 970).—The halogen-derivatives of benzene react with phenylpiperidine, yielding tertiary phenylpiperidine. Tertiary phenylpiperidine is obtained when bromobenzene is heated with piperidine (3 mols.) at 250 — 260° for 24 hours, the product filtered from piperidine hydrobromide and fractioned; also when an alcoholic solution of amidophenylpiperidine is treated with ethyl nitrite and concentrated sulphuric acid. It is a bright yellow liquid of disagreeable odour, boils at 245 — 250° , and is a strong base.

The *platinochloride*, $(C_6NH_{10}Ph)_2 \cdot H_2PtCl_6 + 2H_2O$, crystallises in needles or plates, and is partially decomposed when heated in solution. Mercuric chloride produces an oily precipitate in a hydrochloric acid solution, and potassium dichromate precipitates small, shining, crystalline plates.
F. S. K.

Derivatives of Tertiary Phenylpiperidine. By E. LELLMANN and W. GELLER (*Ber.*, **21**, 2281—2287).—*Orthonitrophenylpiperidine*, $NO_2 \cdot C_6H_4 \cdot C_5NH_{10}$, prepared by heating orthonitrobromobenzene with piperidine, crystallises from alcohol in large, ruby-red prisms, melts at 81° , and is readily soluble in alcohol, ether, benzene, and chloroform. The *hydrochloride*, $NO_2 \cdot C_6H_4 \cdot C_5NH_{10} \cdot HCl$, is a yellow, crystalline compound, and is decomposed by water. The *platinochloride*, $(NO_2 \cdot C_6H_4 \cdot C_5NH_{10})_2 \cdot H_2PtCl_6$, crystallises in shining leaves.

Paranitrophenylpiperidine, $NO_2 \cdot C_6H_4 \cdot C_5NH_{10}$, prepared from parachloronitrobenzene and piperidine, crystallises from alcohol in large, yellow plates, which have a slight blue colour by reflected light, and melt at 105.5° . It is readily soluble in alcohol, chloroform, benzene, and ether. The *hydrochloride*, $NO_2 \cdot C_6H_4 \cdot C_5NH_{10} \cdot HCl$, is a bright yellow, crystalline compound, and is decomposed by water. The *platinochloride*, $(NO_2 \cdot C_6H_4 \cdot C_5NH_{10})_2 \cdot H_2PtCl_6$, forms small, yellow crystals.

Orthoparadinitrophenylpiperidine, $C_6H_3(NO_2)_2 \cdot C_5NH_{10}$, prepared by gradually adding piperidine to finely-divided dinitrochlorobenzene and heating the mixture, crystallises from alcohol in orange-yellow needles with a slight blue colour by reflected light. It melts at 92° , and is readily soluble in ether, benzene, and chloroform.

Parachlororthonitrophenylpiperidine, $NO_2 \cdot C_6H_3Cl \cdot C_5NH_{10}$, the reaction-product of nitroparadichlorobenzene and piperidine, is a bright red, crystalline compound, melts at 51° , and is readily soluble in alcohol, ether, benzene, and chloroform.

Chloronitroamidophenylpiperidine, $NO_2 \cdot C_6H_4Cl(NH_2) \cdot C_5NH_{10}$, is obtained when a concentrated hydrochloric acid solution of stannous chloride is gradually added to a boiling, concentrated hydrochloric acid solution of dinitrophenylpiperidine. It is a crystalline substance, melts at 111.5° , and is soluble in alcohol, benzene, ether and chloroform.

Paramidophenylpiperidine hydrochloride, $NH_2 \cdot C_6H_4 \cdot C_5NH_{10} \cdot 2HCl + H_2O$, prepared by treating paranitrophenylpiperidine with a hot,

concentrated hydrochloric acid solution of stannous chloride, is a yellow compound, and is readily soluble in water and alcohol. Ferric chloride produces a red coloration in a neutral or slightly acid solution of the salt. The free *base* is a colourless, crystalline compound, melts at 40° , and is readily soluble in all ordinary solvents except water; it yields tertiary phenylpiperidine when treated with ethyl nitrite and concentrated sulphuric acid in alcoholic solution. The *hydrochloride* of the acetyl-derivative, $\text{NH}\cdot\text{COMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}_5\text{NH}_{10}\cdot\text{HCl}$, is a colourless, crystalline compound, and readily soluble in water; a subcutaneous dose of 0.3 gram proved fatal to a rabbit within a few minutes. The *acetyl-derivative*, $\text{NH}\cdot\text{COMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}_5\text{NH}_{10}$, crystallises from alcohol in colourless, nacreous plates, melts at 151° , and is readily soluble in alcohol and chloroform, moderately soluble in ether and benzene, but very sparingly soluble in water.

F. S. K.

Formation of Colouring Matters from Paramidophenylpiperidine. By E. LELLMANN and W. GELLER (*Ber.*, **21**, 2287—2288).—Indamines with a bluish or greyish shade are obtained when a cold, neutral solution of a mixture of paramidophenylpiperidine hydrochloride and an equivalent quantity of the hydrochloride of a primary, secondary, or tertiary aromatic amine is oxidised with the theoretical quantity of potassium dichromate, and the colouring matter precipitated with zinc chloride. If oxidation takes place in presence of a metadiamine, for example, metaphenylene- or metatoluylenediamine, intensely blue-coloured substances are produced; and, on adding zinc chloride, these are precipitated in the form of a brown powder. These colouring matters belong to the same group as toluylene-blue, as is shown by the change of colour which occurs when an acid solution is boiled; for example, the toluylene-derivative gives a red, the phenylene colour a more violet dye, both of which are precipitated from concentrated solutions by zinc or sodium chloride. These indamines can be converted into safranines in the usual manner. A safranine which dyes blue is obtained when a mixture of amidophenylpiperidine hydrochloride (1 mol.) and aniline hydrochloride (2 mols.) is oxidised in cold, dilute acetic acid solution.

A blue indophenol separates when a dilute alkaline solution of paramidophenylpiperidine (1 mol.) and phenol (1 mol.) is oxidised with the theoretical quantity of potassium ferricyanide, or when a dilute acetic acid solution of amidophenylpiperidine hydrochloride and phenol is oxidised with ferric chloride. The naphthols yield compounds of a more distinctly violet colour, amongst which that derived from β -naphthol is distinguished by its reddish shade and its solubility in soda.

An intensely blue substance is produced when a hydrochloric acid solution of amidophenylpiperidine is treated with hydrogen sulphide and ferric chloride, and the product precipitated with zinc chloride and sodium chloride. It dyes a somewhat greenish colour in comparison to methylene-blue.

F. S. K.

Orthonitroparahydroxyquinoline and Orthamidoparahydroxyquinoline. By J. ALTSCHUL (*Ber.*, **21**, 2254—2255).—The

nitrohydroxyquinoline described by Matheus (this vol., pp. 851, 965) is identical with the compound obtained by the author (this vol., p. 67) from parahydroxyquinolinecarboxylic acid, and also with the compound obtained by Skraup (Abstr., 1883, 92) from parahydroxyquinoline. The *acetyl*-derivative of amidoparahydroxyquinoline loses water when heated at 235°, and yields a crystalline ethenyl-derivative.

F. S. K.

γ -Hydroxyquinaldine. By M. CONRAD and L. LIMPACH (*Ber.*, **21**, 1965—1984).—*Methyl phenylamidocrotonate*, $C_{11}H_{13}NO_2$, is obtained when equivalent quantities of methyl acetoacetate and aniline are mixed together. It crystallises from methyl alcohol in large, compact prisms, melts at 51°, and, when heated quickly to 240—250°, yields about 40 per cent. of hydroxyquinaldine.

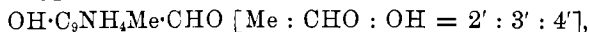
Ethyl quinaldylcarboxylate, $C_{10}NH_8 \cdot COOEt$, is formed when ethyl chloroformate is added to well-dried sodiohydroxyquinaldine suspended in benzene. It crystallises in white, shining prisms, melts at 48°, and is readily soluble in ether, alcohol, and hot benzene, but insoluble in water. It is decomposed into hydroxyquinaldine, carbonic anhydride, and alcohol when heated with water, or more quickly by acids or alkalis. The *platinochloride*, $(C_{13}H_{13}NO_3)_2 \cdot H_2PtCl_6 + 2H_2O$, is a yellow, crystalline compound, and when heated to 100° melts and then solidifies; on further heating, it melts again at 130° with decomposition and evolution of gas.

Quinaldylbenzoate, $C_{10}H_8NO \cdot CPh$, prepared by treating sodiohydroxyquinaldine with benzoic chloride, is very readily soluble in ether, alcohol, and benzene, and crystallises in large, well-defined prisms melting at 129°. It yields benzoic acid and hydroxyquinaldine when warmed with water, or more readily with acids or alkalis. The *platinochloride* is a yellow, crystalline compound, and melts at 180—190° with decomposition.

Sodium hydroxyquinaldineazobenzenesulphonate is formed when γ -hydroxyquinaldine is treated with sodium paradiazobenzenesulphonate in alkaline solution. It crystallises from hot water in orange-red needles, and when warmed with stannous chloride and hydrochloric acid yields sulphanilic acid and amido- γ -hydroxyquinaldine hydrochloride. Amido- γ -hydroxyquinaldine (Abstr., 1887, 680) separates in white, shining prisms when ammonia is added to a solution of this hydrochloride. The constitution of hydroxyquinaldineazobenzenesulphonic acid is therefore $OH \cdot C_9NH_4Me \cdot N_2 \cdot C_6H_4 \cdot SO_3H$ [$N_2 = 3'$].

Thioquinaldine hydrochloride, $C_{10}H_8NS \cdot HCl$, crystallises in white needles, melts at 205—210° with decomposition, and is readily soluble in water.

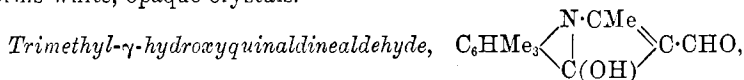
γ -Hydroxyquinaldinealdehyde,



is obtained when chloroform is added gradually to a hot alkaline solution of hydroxyquinaldine and the mixture heated for five to six hours. It crystallises from boiling alcohol in bright yellow, transparent plates, which melt at 273° with decomposition; it is readily soluble in dilute alkalis and concentrated hydrochloric acid, but only sparingly in ether, benzene, or water. The *hydrochloride*,

$C_{11}H_9NO_2.HCl$, dissociates when heated with water. The *platino-chloride* $(C_{11}H_9NO_2)_2.H_2PtCl_6$, is a yellow, crystalline compound; it melts at $215-220^\circ$ with decomposition, and is soluble in hot water. The hydrochloride, $C_{17}H_{15}N_3O.HCl$, of the *hydrazide* crystallises in slender, yellow needles, and is relatively easily soluble in alcohol, but only sparingly soluble in hot water. A condensation product, $C_{21}H_{23}N_3O_3$, is formed in the preparation of hydroxyquinaldinealdehyde. It is soluble in hot benzene and boiling ethyl acetate, and melts at 192° . When heated with water, the larger portion dissolves and γ -hydroxyquinaldine separates from the filtered and concentrated solution.

γ -Hydroxyquinaldine- β -carboxylic acid, $OH.C_9NH_4Me.COOH$ [$= 4' : 2' : 3'$], is readily obtained by oxidising the aldehyde with alkaline potassium permanganate. It is almost insoluble in ether, benzene, and boiling water, but readily soluble in alcohol, and melts at 245° with evolution of carbonic anhydride and formation of γ -hydroxyquinaldine. An aqueous solution of the ammonium salt gives a red coloration with ferric chloride, and yields precipitates with lead acetate, copper sulphate, mercuric nitrate, and silver nitrate. The zinc salt crystallises in needles. The magnesium salt, $(C_{11}H_9NO_3)_2Mg$, forms white, opaque crystals.



is formed when alcoholic chloroform is added gradually to a hot alkaline solution of trimethylhydroxyquinaldine and the mixture heated for several hours. The reaction-product is dissolved in dilute hydrochloric acid and treated with phenylhydrazine hydrochloride, when the hydrochloride of the *hydrazide*, $C_{20}H_{22}N_3O.HCl$, separates as a yellow, crystalline salt, which is sparingly soluble in water and alcohol.

γ -Hydroxyquinaldinesulphonic acid, $C_{10}NH_8O \cdot SO_3H$, prepared by heating γ -hydroxyquinaldine at $110-115^\circ$ with fuming sulphuric acid, crystallises from hot water in long, shining prisms, which contain 2 mols. of water, and are readily soluble in hot alcohol. The anhydrous substance melts at 283° .

The barium salt, $(C_{10}NH_8O \cdot SO_3)_2Ba + 4H_2O$, crystallises from boiling water in large, shining prisms. A dilute, neutral, aqueous solution of the ammonium salt gives precipitates with barium chloride, calcium chloride, lead acetate, and ferric chloride.

Diazo-hydroxyquinaldineanhydride, $C_9NH_4Me < \overset{N}{\underset{O}{\parallel}} N$ [$Me : N : O = 2' : 3' : 4'$], is formed when sodium nitrite is added to a dilute sulphuric acid solution of amidohydroxyquinaldine. It crystallises from ether and benzene in shining, yellow needles, and melts at $129-131^\circ$ with sudden decomposition and evolution of gas. The hydrochloride, $C_{10}H_7N_3O.HCl$, separates as a reddish, crystalline precipitate when hydrochloric acid is added to an ethereal solution of the preceding compound. The hydrochloride of amidohydroxyquinaldine is obtained when a concentrated hydrochloric acid solution of diazo-hydroxyquinaldineanhydride is reduced. Acetantranilic acid is formed when amidohydroxyquinaldine is oxidised with chromic acid.

Amidoquinaldine, $C_9NH_5Me \cdot NH_2$ [$= 2' : 3'$], prepared by heating amidohydroxyquinaldine at $180-210^\circ$ with an acetic acid solution of hydrogen iodide, is a colourless oil which boils at 270° and has a strongly alkaline reaction. The *picrate* is a sparingly soluble, yellow, crystalline compound. The *hydrochloride* is white, crystalline, and very hygroscopic. The *platinochloride*, $(C_{10}H_{10}N_2)_2 \cdot H_2PtCl_6$, is yellow, crystalline, and soluble in hot water.

Nitrochloroquinaldine, $C_9NH_4ClMe \cdot NO_2$ [$Me : NO_2 : Cl = 2' : 3' : 4'$], is obtained when nitrohydroxyquinaldine is heated with a mixture of phosphorus pentachloride and phosphorus oxychloride. It separates from ether or hot benzene in yellowish crystals, is readily soluble in boiling alcohol, sparingly soluble in water, and melts at $93-94^\circ$. It is reconverted into nitrohydroxyquinaldine when gently heated with water.

Nitramidoquinaldine, $NO_2 \cdot C_9NH_4Me \cdot NH_2$ [$Me : NO_2 : NH_2 = 2' : 3' : 4'$], is prepared by saturating a benzene solution of nitrochloroquinaldine with ammonia, adding a small quantity of concentrated alcoholic ammonia and heating the mixture at $180-200^\circ$. It crystallises from alcohol in slender, bright yellow needles melting at 201° .

Diamidoquinaldine hydrochloride, $C_{11}H_{11}N_3 \cdot HCl$, is obtained in colourless crystals when the preceding compound is reduced.

Trichloroquinaldine, $C_{10}H_6NCl_3$, obtained in the preparation of chloroquinaldine (*loc. cit.*), crystallises from alcohol in white needles, melts at 102° , and is soluble in ether.

F. S. K.

Syntheses with Ethyl Acetoacetate. By L. KNORR (*Annalen*, **245**, 357—382; compare *Abstr.*, 1887, 159, 275, and 601).—It was previously mentioned (*Annalen*, **236**, 112) that besides ethyl acetoacetate, methylacetoacetic and benzoylacetic acids form anilides which can be condensed to quinolines.

Methylacetoacetic anilide, $COMe \cdot CHMe \cdot CO \cdot NHPh$, is prepared by heating carefully purified ethyl methylacetoacetate and aniline at $150-160^\circ$. It crystallises from hot water in prisms, melts at $138-140^\circ$, is soluble in ether, benzene, and chloroform, sparingly soluble in hot water.

Dimethylcarbostyryl, [$Me_2 = 3' : 4'$], is obtained on keeping the above anilide dissolved in cold concentrated sulphuric acid for a long time, and may be purified by means of the hydrochloride; it melts at 262° . The *hydrochloride* crystallises from the strong acid solution in long, lustrous needles which give off hydrogen chloride when kept in a desiccator over potash, and are completely decomposed by water. The *sulphate* is decomposed by alcohol. Dimethylcarbostyryl is also a very feeble acid. The *sulphonic acid* is prepared by heating the compound with strong sulphuric acid at 200° . The *barium sulphate* was prepared.

Chlorodimethylquinoline, $C_{11}H_{10}NCl$ [$Cl : Me_2 = 2' : 3' : 4'$], is formed when 3 grams of dimethylcarbostyryl and 5 grams of phosphorus pentachloride are heated at 180° . It melts at 131° , distils with steam, and is a feeble base. The *platinochloride*, $(C_{11}H_{10}NCl)_2 \cdot H_2PtCl_6 + 4H_2O$, forms orange-coloured crystals. When the free base is heated with water at 200° , it is converted into dimethylcarbostyryl.

Dimethylquinoline, [$\text{Me}_2 = 3' : 4'$], is obtained by distilling dimethylcarbostyryl over heated zinc-dust. The product is dissolved in sulphuric acid, extracted with ether, the solution of the sulphate treated with soda, and steam distilled. It melts at 65° , and boils at 290° under 737 mm. pressure. The *hydrochloride* crystallises in prisms; the *platinochloride* (with 2 mols. H_2O) forms flat needles; the *picrate* crystallises in red, lustrous needles, melting at about 205° , the *aurochloride*, *argentonitrate*, and *methiodide* melting at 177° , 180° , and 190 — 191° respectively are also described.

Paradimethylcarbostyryl, [$\text{Me} : \text{Me} = 4' : 3$], (Abstr., 1884, 1198), crystallises in flat prisms of a satiny lustre, and melts at 249 — 250° ; it dissolves very sparingly in ether, chloroform, benzene, and light petroleum, but is soluble in alcohol. It is slightly basic as well as acid. The *hydrochloride* and *nitrate* crystallise in hair-like needles; the *sulphate* forms short prisms; all three salts are decomposed by water. The compound behaves towards bromine-water, phosphorus pentachloride, sodium ethoxide, and methyl iodide just like oxylepidine.

Paradimethylquinoline, $\text{C}_{11}\text{H}_{11}\text{N}$, prepared by distilling 4' : 3-dimethylcarbostyryl with zinc-dust, boils at 280° (under 754 mm. pressure), dissolves readily in alcohol and ether, hardly at all in water, has a burning taste, and a penetrating odour like that of quinoline. The *platinochloride* (with 2 mols. H_2O) crystallises in bent needles which decompose at 231° ; the *picrate* separates in branched needles which decompose at about 230° ; the *aurochloride* forms bright yellow needles and decomposes at about 190° ; the *chromate*, *sulphate*, and *argentonitrate* are described.

Orthodimethylcarbostyryl, [$\text{Me}_2 = 4' : 1$] (*loc. cit.*), crystallises in needles sparingly soluble in water, insoluble in ammonia and alkaline carbonates. The *sodium salt* forms thin plates. The *hydrochloride* and *nitrate* crystallise in needles, and are decomposed by water. The *platinochloride* (with 2 mols. H_2O) was prepared.

Orthodimethylquinoline, [$\text{Me}_2 = 4' : 1$], is a bright yellow oil, readily soluble in alcohol and ether; it has an odour like that of quinoline. The *platinochloride* melts at about 220° with decomposition; the *aurochloride* forms lustrous lozenge-shaped crystals melting at 181° ; the *chromate*, *picrate*, and *argentonitrate* are also described.

Metadimethylcarbostyryl, $\text{C}_{11}\text{H}_{11}\text{NO}$, melts at 220° and dissolves very sparingly in hot water. The *hydrochloride* and *nitrate* crystallise in hair-like needles, and are decomposed by water; the *platinochloride* forms yellow needles which decompose at 233 — 234° .

Metadimethylquinoline, $\text{C}_{11}\text{H}_{11}\text{N}$, boils at about 283° (under 750 mm. pressure). The *platinochloride* (with 2 mols. H_2O) crystallises from hot hydrochloric acid in well-formed, short, reddish-brown prisms which decompose at 227° .

Methyl β -phenylamidophenylacrylate, $\text{C}_{15}\text{H}_{15}\text{NO}_2$, separates in prisms melting at 92 — 93° when a mixture of aniline and methyl benzoylacetate is kept for some weeks at the ordinary temperature.

β -Phenylamidophenylacrylic anilide, $\text{NHPh}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NHPh}$, is formed together with benzoylacetic anilide when the mixture of aniline and methyl benzoylacetate is heated for a long time at 150° . It crystallises in needles, melts at 133° , is almost insoluble in water,

dilute acids, and alkalis, soluble in ether, hot benzene, alcohol, and chloroform. Boiling dilute acids decompose it into aniline and benzoylacetanilide. When distilled, it decomposes into aniline, diphenylcarbamide, and a compound of the formula $C_{15}H_{11}NO$, probably phenylhydroxyquinoline.

Benzoylacetanilide, $COPh \cdot CH_2 \cdot CO \cdot NHPh$, crystallises in plates, melts at $107-109^\circ$, dissolves readily in alcohol, chloroform, and hot benzene, sparingly in hot water and dilute hydrochloric acid. It is dissolved by alkalis, and precipitated by carbonic anhydride. The alcoholic solution gives a blue-violet coloration with ferric chloride. The *isonitroso-derivative*, $C_{15}H_{12}N_2O_3$, crystallises in needles melting at about 190° . When the solution of the anilide in methyl alcohol is saturated with dry hydrogen chloride, the *hydrochloride*, $C_{15}H_{13}NO_2 \cdot HCl$, separates after some hours in lustrous prisms; it melts at 99° , and is extremely soluble in methyl alcohol.

Phenylhydroxyquinoline, $C_{15}H_{11}NO$ (Just, Abstr., 1886, 811), is obtained by heating the above anilide with strong sulphuric acid in a water-bath; a too prolonged heating is to be avoided; no action takes place in the cold. It melts at 254° , dissolves in hot alcohol, readily in alkalis. The alkaline salts are decomposed by carbonic anhydride. The *nitrate* crystallises in hair-like needles; the *hydrochloride* forms splendid needles; the *platinochloride* crystallises in small, lozenge-shaped crystals. When phenylhydroxyquinoline is distilled with zinc-dust, phenylquinoline (Doebner and v. Miller, Abstr., 1883, 1149; and Königs and Nef, Abstr., 1886, 1045), (m. p. 86°), is formed. The *aurochloride*, $(C_{15}H_{11}N)_2 \cdot H_2AuCl_4$, crystallises in needles melting at 204° ; another *aurochloride*, $C_{15}H_{11}N \cdot HAuCl_4$, melting at 160° , was obtained.
N. H. M.

α -Amidolepidine. By C. KLOTZ (*Annalen*, 245, 382—384).— *α -Amidolepidine*, $C_{10}H_{10}N_2$, obtained by the action of alcoholic ammonia on *α -chlorolepidine* at $200-230^\circ$, is a crystalline powder, melts at $131-132^\circ$, dissolves readily in ether, chloroform, alcohol, glacial acetic acid, and hot benzene. The *sulphate* crystallises in needles melting at 155° ; the *picrate* forms sulphur-coloured needles which melt at about 250° ; the *platinochloride* crystallises in orange-coloured needles and melts at 230° .
N. H. M.

Lepidine-compounds. By B. HEYMANN and W. KOENIGS (*Ber.*, 21, 2167—2172; compare this vol., p. 852).—*Orthohydroxybenzyl-lepidine*, $C_6NH_2 \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot OH$, is obtained by reducing orthohydroxybenzylidenelepidine (*loc. cit.*) with hydriodic acid and amorphous phosphorus in glacial acetic acid solution. It crystallises from hot aqueous alcohol in colourless needles, melts at $180-181^\circ$, and is readily soluble in cold absolute alcohol, but only sparingly in dilute alcohol. It dissolves very sparingly in cold, but readily in hot, dilute soda, and a crystalline sodium salt separates from the solution on cooling. The *hydrochloride* is sparingly soluble in cold, very dilute hydrochloric acid, and separates from the hot solution in an oily condition. The *hydrobromide* behaves similarly. Salicylic acid is obtained when the base is fused with alkali and a small

quantity of water, but no hydroxyquinoline-derivative is formed, this is also the case when the para- and meta-compound are treated in the same way.

Meta-amidobenzylidenelepidine, $C_6NH_6 \cdot CH:CH \cdot C_6H_4 \cdot NH_2$, prepared by reducing metanitrobenzylidenelepidine (*loc. cit.*) with stannous chloride and hydrochloric acid in alcoholic solution, crystallises from absolute alcohol in shining, yellow needles or leaves, melts at 141° , and is readily soluble in dilute hydrochloric acid, dilute sulphuric acid, and hot alcohol.

Metahydroxybenzylidenelepidine, $C_6NH_6 \cdot CH:CH \cdot C_6H_4 \cdot OH$, is obtained when a dilute solution of the preceding compound is mixed with sodium nitrite and boiled. It separates from hot, absolute alcohol in brownish-yellow, lance-shaped crystals melting at $254\text{--}255^\circ$, and is sparingly soluble in soda and boiling alcohol. The *hydrochloride* is sparingly soluble in cold, more readily in hot water, and crystallises from hot, absolute alcohol, in which it is readily soluble, in brownish needles.

Metahydroxybenzyllepidine, $C_6NH_6 \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot OH$, prepared by reducing the preceding compound with hydriodic acid and amorphous phosphorus, crystallises from hot alcohol, in which it is sparingly soluble, in prisms melting at 209° . It is rather soluble in cold, dilute soda, and is precipitated from the solution by hydrochloric acid in the form of a sparingly soluble, oily *hydrochloride*. When fused with an alkali, it yields considerable quantities of metahydroxybenzoic acid. Parahydroxybenzyllepidine yields parahydroxybenzoic acid when treated similarly, and a small quantity of paracresol appears also to be formed.

Benzylquinaldine and benzyllepidine, when carefully heated above 350° , distil with only slight decomposition. *Benzyllepidine nitrate* separates from a hot, very dilute nitric acid solution of the base in sparingly soluble crystals. Cinchonic acid is formed in considerable quantity when benzylidenelepidine is boiled for several days with an acetic acid solution of chromic acid.

The melting point of most of the compounds described in the previous paper (*loc. cit.*) are given 4° too high. F. S. K.

Isoquinoline and its Derivatives. By M. LE BLANC (*Ber.*, 21, 2299—2301).—Isoquinoline can be prepared by heating a mixture of homooorthophthalimide and zinc-dust to a dull red heat in a stream of hydrogen. The yield is about 40 per cent. It is also formed when methyl homooorthophthalimide is distilled. γ -Methyl isoquinoline, $C_6H_4 \cdot \begin{smallmatrix} CMe:CH \\ CH=N \end{smallmatrix}$, is obtained by distilling di- or tri-methyl homooorthophthalimide with zinc-dust; it boils at 256° . The *picrate* crystallises in slender needles melting at $194\text{--}195^\circ$. The *platinochloride* is a brownish-red crystalline compound melting at $253\cdot5^\circ$. F. S. K.

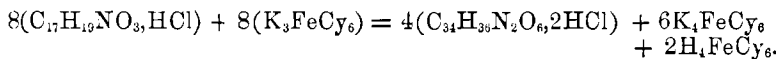
New Vegetable Base. By A. KOSSEL (*Ber.*, 21, 2164—2167).—A new base, $C_7H_8N_4O_2$, which the author names *theophylline*, exists in small quantities in tea extract, and occurs together with *caff  ine*. It crystallises with 1 mol. of water, which it loses at 110° , is considerably

more soluble in alcohol and water than theobromine, and is extremely soluble in very dilute ammonia. It melts at 264° , forms crystalline salts with hydrochloric acid, nitric acid, platinum tetrachloride, auric chloride, and mercuric chloride, and combines with soda to form a readily soluble compound. When thiophylline is evaporated with chlorine-water, a scarlet residue is obtained, which changes to violet when treated with ammonia.

The *silver-derivative*, $C_7H_7N_4O_2Ag$, obtained in the form of an amorphous precipitate by adding silver nitrate to an aqueous solution of the base, crystallises from hot ammonia, and is readily soluble in nitric acid. The *methyl-derivative*, $C_8H_{10}N_4O_2$, prepared by heating the silver-derivative with methyl iodide and methyl alcohol, melts at 229° , and is identical with caffeine. Thiophylline is, therefore, dimethylxanthine.

F. S. K.

Morphine. By O. HESSE (*Pharm. J. Trans.*, **18**, 801).—The author questions the accuracy of the formula $8C_{17}H_{19}NO_3 + 9H_2O$, assigned to crystalline morphine by Dott (this vol., p. 506), as his own experiments have shown exactly 1 mol. H_2O for each molecule of morphine. The melting point, according to his observations, is 230° (with decomposition), instead of 120° , as stated in the books. In the delicate test for morphine proposed by Armitage (this vol., p. 1137) the reaction is not the result of reduction of the ferric chloride, but of the formation of pseudomorphine and ferrocyanic acid, thus:—



Pseudomorphine is actually deposited if the solution is not too dilute, and this substance being somewhat soluble in water, is the cause of the blue coloration in the presence of ferric chloride.

R. R.

Narcotine. By W. ROSER (*Annalen*, **245**, 311—326).—*Iodotarconine methiodide*, $C_{11}H_8INO_3, MeI$, is obtained together with tarconine methiodide when narcotine dissolved in 20 parts of 80 per cent. alcohol, and some hydrochloric acid is treated with the corresponding amount of iodine in three portions, and boiled in a reflux apparatus for 10 hours. The periodide which separates is dissolved in water, and treated with hydrogen sulphide. The liquid is warmed and quickly filtered, by which a separation of the sparingly soluble iodotarconine methiodide from the more readily soluble tarconine methiodide is effected. It is almost insoluble in boiling alcohol, and crystallises from hot water in three forms. When heated with a solution of iodine, the *periodide*, $C_{11}H_8INO_3, MeI, I_2$, is obtained. This crystallises in sparingly soluble, dark, lustrous needles melting at 171° .

Iodotarconine methochloride, $C_{11}H_8INO_3, MeCl + H_2O$, prepared by treating an aqueous solution of the iodide with silver chloride, crystallises from alcohol in yellowish needles. The *platinochloride*, $(C_{12}H_{11}INO_3)_2, PtCl_4$, crystallises in short, lustrous prisms; the *aurichloride* forms slender, yellow needles; the *mercurichloride* crystallises in long needles.

Iodotarconine, $C_{11}H_9INO_3 + H_2O$, is formed when iodotarconine methochloride is heated gradually up to 180° . It crystallises from water in yellowish-red needles. The anhydrous compound is dark-red. The *hydrochloride*, $C_{11}H_9INO_3 \cdot HCl + 2H_2O$, crystallises in yellow needles of silky lustre.

Tarconine methiodide, $C_{11}H_9NO_3 \cdot MeI$, prepared as described above, crystallises in groups of long, yellow needles; it combines with iodine with formation of the *periodide*, $C_{11}H_9NO_3 \cdot MeI \cdot I_2$; it crystallises from alcohol in long, red-brown needles melting at 160° (compare Jörgensen, *J. pr. Chem.* [2], 2, 433). When 1 gram of methyltarconine chloride is heated with 7 grams of strong hydrochloric acid for four hours at 140 – 150° , a compound, $C_{11}H_9NO_3 \cdot HCl + 1\frac{1}{2}H_2O$, probably tarconine hydrochloride (Wright, *Trans.*, 1877, 535), and methyl chloride are formed.

Methyltarconic acid, $C_{11}H_{11}NO_2$, is formed together with formaldehyde when the solution of the ammonium base obtained by the action of silver oxide on tarconine methochloride is boiled; it separates in small, lustrous crystals. It is insoluble in alcohol, almost insoluble in water, readily soluble in mineral acids, and in alkalis (not ammonia). The *hydrochloride* crystallises in slender, lustrous needles, very readily soluble in water, sparingly in alcohol. The *sulphate*, $(C_{11}H_{11}NO_2)_2 \cdot H_2SO_4 + 6H_2O$, and the *acid sulphate*, $C_{11}H_{11}NO_3 \cdot H_2SO_4 + 3H_2O$, crystallise in small, yellow crystals and white prisms.

Bromotarconine methobromide, $C_{11}H_9BrNO_3 \cdot MeBr + H_2O$, is prepared by adding bromine-water to an aqueous solution of tarconine methochloride, and decomposing the perbromide which separates with hydrogen sulphide. It first separates in a labile form, in long sulphur-coloured needles; these gradually change to flat prismatic crystals.

The *perbromide*, $C_{11}H_9BrNO_3 \cdot MeBr \cdot Br_2$, crystallises in lustrous, gold-coloured plates, melts at 165° , and is converted by boiling with alcohol into the bromide just described.

Bromotarconine methochloride, prepared by digesting the bromide with silver chloride, crystallises in slender needles, very readily soluble in alcohol, less in water. The *platinochloride* is yellowish-red; the *aurochloride* forms slender yellow needles.

Methylbromotarconic acid, $C_{11}H_{10}BrNO_3$ (v. Gerichten, *Abstr.*, 1883, 869), is formed as barium salt when bromotarconine methobromide is treated with silver oxide, and the whole boiled with baryta. It melts at 233° .

N. H. M.

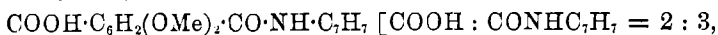
Papaverine. By G. GOLDSCHMIEDT (*Monatsh.*, 9, 327–348; compare *Abstr.*, 1886, 83, 478; 1887, 163; this vol., p. 302) —Crystalline papaverine benzyl chloride (30 grams) is oxidised with 2 per cent. potassium permanganate (100 grams) at 40 – 45° , and the solution filtered. The filtrate contains veratric acid ($7\frac{1}{2}$ grams) and small quantities of benzoic and oxalic acids. The residue is either extracted consecutively with boiling water and alcohol, or suspended in water, and the oxide of manganese dissolved by passing a stream of sulphurous anhydride. The mixture of organic compounds is warmed with dilute hydrochloric acid and the solution filtered; on

adding ammonia to the filtrate, papaveraldine is precipitated. The residue contains a compound melting at $153-154^{\circ}$ (see below), benzylhemipinisoimide, and a very small quantity of a compound melting above 240° which was not obtained in the pure state.

The substance melting at $153-154^{\circ}$ is *benzylpapaveraldine-ammonium hydroxide*, $C_7H_7 \cdot C_{20}H_{19}NO_5 \cdot OH$, or *oxide* $(C_{20}H_{19}NO_5 \cdot C_7H_7)_2O$. It crystallises from boiling water or alcohol in small, slender, colourless needles, and is readily soluble in cold glacial acetic acid, acetone, chloroform, and benzene, but rather sparingly soluble in ether. It dissolves in boiling concentrated hydrochloric acid, yielding a yellow solution from which yellow needles of papaveraldine hydrochloride separate on cooling; it also dissolves in cold sulphuric acid, forming a colourless solution which shows the characteristic colour reaction of papaveraldine when heated. The *hydrochloride* crystallises in slender, yellow needles, but it quickly decomposes when dry and loses its acid.

Benzylhemipinisoimide, $C_{17}H_{15}NO_4$, crystallises from alcohol in slightly yellow needles, melts at 225° , and sublimes without decomposition. It is a neutral substance, and is not dissolved by acids or alkalis. It yields hemipinic acid and benzylamine when boiled for a long time with potash (sp. gr. 1.15), but when the reaction is interrupted after a short time benzylhemipinamic acid is obtained.

Benzylhemipinamic acid,



or 3 : 2 and $(OMe)_2 = 4 : 5]$, crystallises from alcohol in very slender needles, and is, as a rule, more readily soluble than the imide. It loses water when heated, and is converted into the imide, so that it has the same melting point as the latter. It is readily soluble in alkalis and ammonia, but when an ammoniacal solution is evaporated the imide is obtained. The *potassium* salt crystallises in white needles, and is readily soluble in water. The *silver* salt is amorphous. The *lead* salt crystallises in microscopic, rhombic plates. The *calcium* salt, $(C_{17}H_{15}NO_5)_2Ca$, crystallises in small needles, and is rather easily soluble in water.

Veratric acid and papaveraldine, together with small quantities of acetic and oxalic acid, are obtained when papaverine ethobromide is oxidised with potassium permanganate, and the reaction products separated as described above, but the chief product is ethylhemipinisoimide. No compound analogous to benzylpapaverine-ammonium hydroxide (or oxide) is formed.

Ethylhemipinisoimide, $C_{12}H_{13}NO_4$, crystallises from boiling alcohol, in which it is only sparingly soluble, in yellowish needles, melts at $226-227^{\circ}$, and sublimes in colourless needles.

Ethylhemipinamic acid, $C_{12}H_{13}NO_5$, is formed when the preceding compound is heated with potash for a short time. It loses water when heated, and melts at the same temperature as the imide. The salts are similar to those of the corresponding benzyl-derivative.

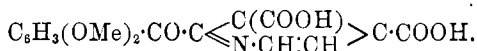
Hemipinic acid and ethylamine are obtained when ethylhemipinisoimide is boiled for a long time with potash. Hemipinic acid and cinchomeronic acid are formed when dimethoxyquinoline (compare Goldschmiedt, this vol., p. 302) is oxidised with 4 per cent.

alkaline potassium permanganate. This dimethoxy-compound is therefore a derivative of isoquinoline.

The acid described as dihydroxycinchonic acid (Abstr., 1886, 478) yields a yellow, crystalline substance, when heated above its melting point until gas is no longer evolved; the product is sparingly soluble in water, melts at 230° , and gives a reddish-violet iron reaction. It yields isoquinoline when distilled with zinc-dust.

F. S. K.

Constitution of Papaverine. By G. GOLDSCHMIEDT (*Monatsh.*, **9**, 349—360).—Papaverine is a derivative of isoquinoline; it contains the two groups, dimethoxyisoquinoline, $\langle \begin{smallmatrix} \text{N}:\text{CH}- \\ \text{CH}:\text{CH} \end{smallmatrix} \rangle \text{C}_6\text{H}_2(\text{OMe})_2$ [$(\text{OMe})_2 = 1 : 2$ or $3 : 4$], and dimethylhomocatechol, which are most probably united by the CH_2 -group of the latter. The constitution of papaverine is therefore probably $\text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{CH}_2 \cdot \text{C} \langle \begin{smallmatrix} \text{C}_6\text{H}_2(\text{OMe})_2 \\ \text{N}:\text{CH}:\text{CH}- \end{smallmatrix} \rangle$, [$(\text{OMe})_2 = 1 : 2$ or $3 : 4$], and in accordance with this view papaveraldine has the constitution $\text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{CO} \cdot \text{C} \langle \begin{smallmatrix} \text{C}_6\text{H}_2(\text{OMe})_2 \\ \text{N}:\text{CH}:\text{CH}- \end{smallmatrix} \rangle$, and papaverinic acid the constitution



F. S. K.

Cocaine and its Salts. By B. H. PAUL (*Pharm. J. Trans.* [3], **18**, 781—785).—Ready crystallisability was pointed out by Lossen and Wöhler as a characteristic property of pure salts of cocaine, and this is confirmed by the author, who also rejects Stockman's hypothesis that the uncrystallisable portion of cocaine hydrochloride is a solution of cocaine in hygrine. Hygrine he regards as a mythical substance, contending that the true explanation is, that an amorphous alkaloid is associated with cocaine in the coca leaves. He has obtained this alkaloid in quantity sufficient for a detailed examination, and in the meantime states that it has a yellow colour and a bitter taste, and that it produces only a very slight anæsthetic effect on the tongue, but not until after the lapse of several minutes. Its hydrochloric acid solution on evaporation leaves a gummy residue without any sign of crystallisation, and ammonia, whilst failing to produce in it the precipitate of needle-shaped crystals characteristic of pure cocaine, causes the liquid to become milky, and soft clots to separate. The amorphous alkaloid has a peculiar smell like benzoïn and butyric acid, and when it is heated with hydrochloric acid in a sealed tube benzoic acid is formed.

R. R.

Ptomaines. By O. DE CONINCK (*Compt. rend.*, **106**, 1604—1605).—The ptomaine $\text{C}_8\text{H}_{11}\text{N}$ (this vol., p. 730) forms two mercurichlorides, one of which, $(\text{C}_8\text{H}_{11}\text{N}, \text{HCl})_2 \cdot \text{HgCl}_2$, crystallises in small, white needles slightly soluble in water and in dilute alcohol, but insoluble in absolute alcohol. It decomposes when exposed to moist air. The other is a sesqui-salt, $(\text{C}_8\text{H}_{11}\text{N}, \text{HCl})_2 \cdot 3\text{HgCl}_2$, and forms long, yellowish

needles, which are insoluble in the ordinary solvents, and decompose when exposed to moist air.

The methiodide crystallises in slender, white needles, which alter very slowly when exposed to the air, and dissolve in all proportions in absolute alcohol. With alcoholic potash, it gives a deep red coloration, which is intensified by hydrochloric or acetic acid, but is destroyed by a slight excess of ammonia. The liquid acquires no fluorescence. If the methiodide is heated with solid potash and a small quantity of water, a garnet-red coloration is produced, and on more strongly heating, an odour of pyridine dihydride is evolved. If the methiodide is distilled with aqueous potash, the distillate has a red colour, and when exposed to the air becomes highly fluorescent. In some cases, the red coloration rapidly changes to dull green, owing to the reducing action of the ptomaine which is liberated towards the end of the process. Only a very slight excess of ammonia is required to destroy the red coloration, and in this respect the ptomaine differs from the methiodides of the coal-tar pyridines and of the bases obtained from cinchonine and brucine. It is evident, however, that in its general behaviour this ptomaine resembles the pyridine bases.

C. H. B.

Alkaloids in Human Urine. By J. L. W. THUDICUM (*Compt. rend.*, 106, 1803—1806).—The urine was mixed with 5 per cent. of sulphuric acid previously diluted with twice its own volume of water, and the alkaloids were precipitated by phosphomolybdic or phosphotungstic acid. The precipitate was washed, treated with barium hydroxide and barium carbonate, care being taken to avoid an excess of hydroxide, and the deep red solution thus obtained was filtered. If ferric chloride is added to the red liquid, it produces a bulky precipitate, which contains *urochrome*, the colouring matter of the urine in combination with iron. This *urochrome* may be isolated in several different ways, and then treated with sulphuric acid, or the precipitate may be treated directly with the acid. In either case, the product answers to the description given by Proust in 1881. It is a deep, violet-red, bulky precipitate, which when treated with ether yields a resin and a mixture of *omicholin* and *omicholic acid*. The portion insoluble in ether consists of a red compound, *uropittin*, soluble in alcohol, and a black resin, *uromelanin*.

Omicholin has approximately the composition $C_{24}H_{38}NO_5$, and is a red, resinous substance, insoluble in ammonia, but soluble in ether and alcohol. Its solution shows a bright green fluorescence, and gives an absorption-spectrum consisting of a band between D and E.

Omicholic acid has the composition $C_8H_{22}NO_4$, and is also a resinous, red substance soluble in ether or alcohol, forming a solution which shows a green fluorescence and gives an absorption-band between D and E. This band is, however, narrower than the band given by *omicholin*. *Omicholic acid* is soluble in ammonia, and is reprecipitated by acids.

Uropittin was not obtained pure. It is always mixed with one or other of its modifications, *meta-uropittin* and *uro-rubin*, and is partially altered by contact with the oxygen of the air. It contains

11 per cent. of nitrogen. Its alcoholic solution is red, and gives an absorption-band at F.

Uromelanin has the composition $C_{36}H_{43}N_7O_{10}$, and is insoluble in alcohol or ether, but dissolves in dilute solutions of the alkalis, from which it is precipitated by acids. With silver, barium, calcium, lead, and zinc it forms basic and acid salts. The silver salt has the composition $C_{36}H_{40}AgN_7O_9$. *Uromelanin* is a very stable substance; the quantity excreted by an adult is 0.3 to 0.5 gram per day.

Neither urochrome nor any of the other products can be obtained crystallised. *Urochrome* is an alkaloid, the function of which is as yet unknown. The products of its decomposition are not related to the colouring matters of the blood or of the bile.

If the filtrate from the urochrome iron precipitate is concentrated, it yields bulky crystals which may be purified by recrystallisation from alcohol. These consist of an alkaloid, *uro-theobromine*, isomeric with ordinary theobromine. It sublimes without change, forms no crystalline precipitate with silver nitrate, and displaces acetic acid from cupric acetate, forming an insoluble compound.

Creatinine is also present, and the mother-liquor from the creatinine contains three alkaloids. *Reducine*, $C_{12}H_{26}N_6O_9$ or $C_6H_{11}N_3O_4$, forms a barium compound which is almost insoluble in alcohol. Neutral or acid solutions of *reducine* reduce ferric, cupric, or mercuric salts to ferrous, cuprous, or mercurous salts respectively, and silver salts to metallic silver. *Para-reducine* unites with zinc oxide to form a compound, $C_6H_9N_3O \cdot ZnO$ or $C_6H_9ZnN_3O_2$. *Aromine* could not be isolated in a pure condition. When heated, it gives off an aromatic odour resembling that obtained from tyrosine under similar conditions.

C. H. B.

Oxidation of Albumin with Permanganate. By R. MALY (*Monatsh.*, 9, 255—283; compare Abstr., 1885,824).—The author has previously described an oxyprotosulphonic acid obtained by oxidising albumin with permanganate. On further treatment with permanganate, this acid is converted into *peroxyprotic acid*. Like all albuminous bodies it gives the biuret reaction, contains sulphur, and its carbon and nitrogen are present in the same ratio as in albumin, from which it differs in not being precipitated by a solution of potassium ferrocyanide containing a little acetic acid, or by tannic acid. *Baryta* readily decomposes the acid with formation of the following substances:—Oxalic, sulphurous, isoglyceric, amidovaleric, benzoic, formic, and glutamic acids, leucine, ammonia, and traces of pyrroline.

G. T. M.

Physiological Chemistry.

Coagulation of the Blood. By J. B. HAYCRAFT and E. W. CARLIER (*Brit. Med. Jour.*, 2, 1888, 229—232).—The blood was received directly from the finger-tip into a tall, cylindrical vessel filled with viscid castor-oil. By occasionally inverting the vessel the blood may be kept from coming in contact with the sides or ends of the vessel for a considerable time. Blood removed in this way from the body remains uncoagulated for an hour or more. Not only is its fluidity preserved, but the white corpuscles remain rounded in shape, and the blood plates do not tend to run together or change in any way. As soon, however, as the blood comes in contact with solid matter, other conditions remaining the same, the white corpuscles exhibit amœboid movement (if the temperature is high enough), fibrin is formed, and the blood plates become adhesive. The conclusion is drawn that all these changes result from the mechanical stimulation of living and naked protoplasm by solid matter. Actual disintegration leading to the disappearance of the white corpuscles was not observed, but the following were the appearances noted:—The coarsely granular corpuscles became flattened and irregular in outline, due to amœboid movement. They then lost their granules, or these retired to one part of the cell, the rest of the cell becoming clear. The strings of fibrin would then be seen gradually forming. The finely granular corpuscles were observed to present the same appearance, with the exception that their fine granules did not congregate to such an extent. The production of fibrin ferment from the white corpuscles, and probably also from the blood plates, which are regarded as pieces of undifferentiated protoplasm, is regarded not so much as a result of death and disintegration, as of living metabolism in those structures. W. D. H.

Alcaptonuria. By R. KIRK (*Brit. Med. Jour.*, 2, 1888, 232—233).—A certain kind of human urine darkens on the addition of alkalis. Bödeker (*Annalen*, 117, 98) isolated from such urine a substance to which he gave the name "alcapton." Ebstein and Müller (*Virchow's Archiv*, 62, 554) found, as they supposed, catechol, and Smith (*Dublin Med. Jour.*, 73, 465) protocatechuic acid. In a former paper (*Brit. Med. Jour.*, 2, 1886, 1017), the author showed that the substance differs somewhat in its reactions from both those compounds, and gave it the name urrhodinic acid. Further investigation has shown that a mixture of two substances is in reality present, one which is precipitable by neutral lead acetate, and one which is not. The former is called *uroleucic acid*; this is soluble in water, alcohol, and ether; it crystallises from ether in stellate groups; it has a strongly acid reaction, reduce Fehling's solution and Löwe's bismuth solution. The crystals melt at 133°3', and have the formula $C_9H_{10}O_5$. A solution gives with ferric chloride (1 in 40) a transient, green colour; a drop of the ferric solution added to the crystals produces a red colour.

The substance which is not precipitated by lead acetate is amorphous and has an acid reaction. It exercises the same general reducing reactions, but these are not so keen, and in fact it corresponds in all its properties with Bodeker's alcapton. It is provisionally termed uroxanthic acid.

W. D. H.

Action of Artificial Dyes on the Animal Organism. By T. WEYL (*Ber.*, 21, 2191—2192).—Naphthol-green B has no injurious effects on dogs when administered directly into the stomach in daily doses of 1 to 2 grams for 14 days. Dinitrocresol (compare this vol., p. 529) is poisonous. Martius'-yellow (dinitro- α -naphthol), which is not fatal to rabbits (compare this vol., p. 184), is poisonous to dogs of medium size, even in small doses. 0.5 gram was injected into the stomach of a dog weighing 6850 grams, on two consecutive days, and on the third day 1 gram of the sodium salt; the animal died after the last injection.

Subcutaneous doses of 0.1 gram daily for four days, or two doses of 0.2 gram, killed a dog weighing 8800 grams. Naphthol-yellow S (sulphonic acid of Martius'-yellow) is quite uninjurious even in doses four times as large as fatal doses of Martius'-yellow. Aurantia is probably poisonous, but up to the present time no azo-dye is known to be poisonous. Three commercial samples of safranine proved fatal when administered in three subcutaneous doses of 0.5 gram of the hydrochloride to dogs weighing 5 to 6 kilos.

F. S. K.

Chemistry of Vegetable Physiology and Agriculture.

Bacteriological and Chemical Investigation of some Bacilli.
By J. KUNZ (*Monatsh.*, 9, 361—377).—*Bacillus strumitis* was found by Tavel in two cases of *struma cystica*, both patients having suffered intense intestinal catarrh; it also occurs in animals. Its length varies from 1 to 1.5 μ , and its breadth from 0.5 to 0.6 μ . It thrives well in Koch's peptone gelatin; in agar-agar jelly—especially in presence of sugar, growth is very rapid, and a large quantity of gas is evolved, but in no case is any particular odour perceptible. It is extremely mobile, and is best stained with alkaline methylene-blue by Löffler's method. When 140 grams of inoculated gelatin, containing 2 per cent. of grape-sugar, are kept for three days at the ordinary temperature, and finally for 12 hours at 32°, 0.0149 gram of pure carbonic anhydride is evolved. Lactic acid and succinic acid are produced when it is grown in nutrient gelatin containing 5 per cent. of grape-sugar. 1500 grams of the solution gave 1.57 gram of succinic acid and 1.77 gram of zinc lactate. It grows in milk without causing coagulation or change of reaction.

Bacillus pyocyaneus, the cause of the colour in blue and green pus, is 3.2 μ long and 0.8 μ broad on the average. Inoculated gelatin kept for three to four days at the ordinary temperature, and then for seven

days at 35°, liquefies in a few days, shows a green fluorescence, and has the specific smell of blue pus. Pyocyanin and pyoxanthose were both isolated from the solution, but the liquid still showed a green fluorescence due to a distinct colouring matter which is only soluble in water and alcohol, and is not destroyed by boiling. Concentrated solutions of this colouring matter transmit red and green light only, but dilute solutions have no absorptive power. Only a few centigrams of pure pyocyanin were obtained from 6 kilos. of the solution; it contains nitrogen and sulphur, and is not hygroscopic. The green pigment which is formed when this bacillus is grown in nutritious gelatin is very probably produced by the oxidising action of the air on a chromogen which is formed by the bacillus, as the pigment is not contained in the bacterial cells. In gelatin solutions, the green colour disappears gradually at the ordinary temperature in 10 to 15 weeks, giving place to a dark, reddish-brown shade, and the reaction becomes strongly alkaline. The bacillus grows in milk, and produces a yellowish-green solution which becomes intensely green when ammonia is added.

The cells of *Bacterium phosphorescens* are almost circular, being 1.3 to 1.9 μ long and 1.1 to 1.7 μ broad; each cell is mobile and surrounded by a clearly perceptible zooglœa membrane; sometimes two are united. It grows slowly at the ordinary temperature in peptonised gelatin or in peptonised gelatin containing 2 per cent. of grape-sugar, but only at the surface, and the property of emitting light seems to be dependent on the presence of oxygen. It grows well in 2, 3, and 4 per cent. solutions of sea-salt, containing 0.25 per cent. of peptones, forming thick rods 2 to 2.9 μ long and 0.9 to 1.2 μ thick on the average. These solutions are very phosphorescent, far more so than any inorganic substances or an alkaline amyl alcohol solution of lophin; on shaking, the phosphorescence becomes more clearly apparent, but on cooling to 0° its intensity is slightly diminished. The phosphorescence disappears when the solution is heated at 35° for a few minutes, but reappears on cooling; it is, however, completely destroyed by heating at 35° for 15 minutes. After two to three weeks, the solutions become yellowish and gradually lose their phosphorescence; after several weeks, phosphorescence ceases entirely, but the bacteria do not die. The solutions phosphoresce equally well if placed in the dark immediately after inoculation. The phosphorescence is most probably caused by some vital process, as it is destroyed by all reagents which kill the protoplasm of the cells.

Bacterium phosphorescens grows in 3 per cent. solutions of sodium chloride, magnesium sulphate, or sodium sulphate containing 0.25 per cent. of peptones, and the solutions show intense phosphorescence. It also grows in urine and in milk.

Koch's comma bacillus grows very quickly in a solution prepared from serum albumin and fresh pancreatic glands, and the solution soon becomes turbid. 3 litres of such a solution were kept for three days at 35°, and then treated by Brieger's method. 0.01 gram of the ptomaine obtained was injected subcutaneously into a frog, but without any apparent result; the same quantity injected into a mouse proved fatal in two hours. A subcutaneous dose of 0.02 gram was

given to a rabbit weighing 1100 grams; after two hours, the action of the salivary glands was greatly stimulated, and diarrhœa set in, but the animal ultimately recovered. A non-poisonous base was separated from the ptomaine; its platinochloride, $(C_2H_5N)_2, H_2PtCl_6$, is sparingly soluble in water, and when treated with soda gives off a smell very similar to that of human semen. (Compare Schreiner, Abstr., 1879, 72. and Ladenburg and Abel, this vol., p. 441.)

Small quantities of succinic acid are formed by the growth of the comma bacillus, but lactic acid is not produced. F. S. K.

Cultivation of Bacillus Lepræ. By B. RAKE (*Brit. Med. Journ.*, 2, 1888, 215—221).—As a result of numerous experiments carried out at the Trinidad Leper Asylum, the following conclusions are drawn:—

1. At a tropical temperature, *Bacillus lepræ* does not grow on the ordinary nutrient media.

2. In all animals yet examined, inoculation or feeding with leprous tissues is not followed by local growth or general dissemination of the bacillus.

3. When the bacillus is placed in putrid fluids or buried in the earth, it also does not multiply. W. D. H.

Unicellular Algæ. By V. JODIN (*Ann. Agronom.*, 14, 241—255).—The author has made cultivations of various species of *Protococcus*, *Zygnema*, &c., in artificial media, consisting of solutions of the requisite minerals in distilled water. The most suitable solution is the same as that used by Raulin in his experiments on *Aspergillus niger*. The solution is placed in flasks which are exposed to the light; the carbonic anhydride is renewed in the air of these flasks by an automatic generator. This simply consists of a flask filled with a solution of ferric oxalate, connected with the culture flask by a bent glass tube passing through the caoutchouc stopper of the latter. The ferric oxalate evolves carbonic anhydride on exposure to light. Under favourable circumstances the crop obtained in several weeks' exposure amounts to 10 grams of fresh algæ or 1 to 2 grams of dried product per litre. These cultivations are well adapted to throw light on the chemical processes taking place in the green cell, since the crops obtained are uniform and homogeneous and free from the disturbing influences arising from the differentiation of organs and the migration of proximate principles in the higher plants. Moreover these algæ live completely immersed in water. As regards phosphoric acid, the author finds that its percentage varies from 0.5 to 3.0 of the dry matter, being greatest when the nutritive medium is rich in phosphoric acid. Although the living cell has the power to exhaust the solution of phosphoric acid, yet the same cell dried over sulphuric acid, and consequently with its physiological activity impaired or destroyed, yields up to water in which it is macerated nearly all the phosphoric acid previously assimilated. The proportion of nitrogen in *Protococcus* varies from 1.43 to 6.67 per cent. of the crop. The conditions of assimilation of this element are still under experiment.

J. M. H. M.

Influence of Compressed Oxygen on the Growth of Plants.

By S. JENTYS (*Ann. Agronom.*, 14, 275—278).—The experiments were made in an apparatus belonging to the University of Tübingen, and the gases, after being carefully purified, were compressed by the aid of the town water supply which is delivered at 7·5 atmospheres. Young plants of beans, sunflower, peas, buckwheat, radish, &c., were chosen, the length of the shoot above a fixed mark carefully noted, and the subsequent growth in the gases employed measured or observed through a horizontal microscope. Errors due to heliotropic curvature were avoided by surrounding the apparatus with a black curtain. The general results are that growth is in no case completely arrested by increase in the pressure of oxygen above the atmospheric pressure, but it is always retarded, and the more so the greater the pressure, provided the duration of the experiments is the same. Peas are more sensitive than beans, and beans than sunflowers. As regards pressures equal to or less than the atmosphere, the augmentation of the partial pressure of oxygen up to one atmosphere is decidedly favourable to the growth of the radish, white mustard, and turnip; it is almost without influence on that of the bean, sunflower, and pea. Carefully purified oxygen at atmospheric pressure shows no injurious influence at the end of three days' exposure. Compressed air retards growth, but the retardation is due to increased pressure of the nitrogen, since plants grow more slowly in air compressed to 5 atmospheres than in pure oxygen at the atmospheric pressure. The influence of mixtures of compressed hydrogen and nitrogen with oxygen at its normal pressure in the air is always unfavourable. Respiration and growth are in general affected both in the same direction by alteration of pressure. The injurious influence of oxygen above atmospheric pressure is not due to any inability to support respiration, but to some actively poisonous influence exerted after a time by the gas at high pressures.

J. M. H. M.

The Rôle of Oxygen in Plant Life. By W. PALLADIN (*Ann. Agronom.*, 14, 278—279, from *Bull. Soc. Imp. Nat. Moscow*, 1886, 44—133).—The principal sign of fermentation, or life without oxygen, is the greater expenditure of material than takes place under normal circumstances in the air. Experiments made by the author on the young roots of germinating beans bring the intramolecular respiration of the higher plants under this formula. The cuttings of roots 2 centimetres in length lost 4·6 per cent. of their dry weight during normal respiration in the air for 20 hours, and more oxygen was absorbed than was given out again as carbonic anhydride. Placed for 20 hours in a gas deprived of oxygen, the same roots lost 11 per cent. of their weight, in spite of the gradual slackening of the vital phenomena. The carbonic anhydride evolved was 0·55 of the loss of weight, proving that this gas is not the sole volatile product of intramolecular respiration.

J. M. H. M.

Decomposition of Carbonic Anhydride by Plants deprived of Chlorophyll. By HUEPPE (*Ann. Agronom.*, 14, 274).—In this note, the idea is advanced that certain plants deprived of chlorophyll,

such, for example, as one of the nitrifying (?) bacteria mentioned by Heraeus, are capable of decomposing carbonic anhydride, and employing the carbon for the synthesis of carbohydrates. For example, carbonate of ammonia is stated to be decomposed by the bacterium in question with formation of ammonia, aldehyde, and nascent oxygen. The aldehyde is built up into carbohydrates, and the nascent oxygen nitrifies the ammonia to nitric acid. J. M. H. M.

Formation of Starch by Plants from Organic Solutions. By E. LAURENT (*Ann. Agronom.*, 14, 273—274).—The author's results on this subject agree with those of A. Meyer, and were obtained during the same year. He employed etiolated shoots of potato plants in which the reserve material was exhausted, and not a trace of starch could be found in sections taken at different heights. They were plunged in solutions of a great number of different organic compounds, of degrees of concentration varying from 0.2 to 20 per cent., and placed in a dark place. Only seven compounds were transformed into starch, namely, glycerol, dextrose, lævulose, galactose, saccharose, lactose, and maltose. Only in very rare cases was there any growth without formation of starch. Whether any of the substances were utilised for respiratory purposes without either formation of starch or growth of the stem, is an undetermined point. J. M. H. M.

Formation of Organic Acids in Growing Plants. By W. PALLADIN (*Bied. Centr.*, 1888, 499).—The author shows that during the exhalation of plants, the ratio $\text{CO}_2 : \text{O}_2$ is less than unity; and he calculates, using Lieberkühn's formula, that when all the nitrogen of the albumin has been converted into asparagine that there remains a residue containing no oxygen; this residue must either be oxidised, or else must be absorbed in the formation of cellular tissue, but in either case this change must be accompanied by a strong assimilation of oxygen whereby $\text{CO}_2 : \text{O}_2$ becomes less than 1. By the transformation of asparagine and carbohydrates into albumin, a strongly oxidised residue must remain, and acids are a bye-product from such regeneration; it is also considered that the water produced by exhalation is a product of regeneration. E. W. P.

Formation of Crystals of Calcium Oxalate in Plant Cells. By J. H. WAKKER (*Ann. Agronom.*, 14, 274—275, from *Bot. Centr.*, 33, 360).—According to the author, the crystals are not formed in the mass of protoplasm, but in the cell sap, and are always found in the vacuoles. J. M. H. M.

Influence of Magnesium and Calcium Chlorides on Germination. By R. HINDORF (*Bied. Centr.*, 1888, 461—462).—The injury which follows the application of Stassfurth waste salts to plants arises from the chlorine present, but then only when the salts are in too great quantity. Germination of wheat, rye, barley, oats, peas, &c., is assisted by these salts. The sulphates also are injurious, but not to such an extent as the chlorides. E. W. P.

Glutinous Rice of Japan. By SHIMOYAMA-YUNICHIRO (*Ann. Agronom.*, 14, 287—288, from *Bot. Centr.*, 32, 6).—There are many varieties of glutinous rice in Japan. Besides ordinary starch, the starch of the Mozi rice consists of soluble starch, dextrin, and perhaps maltose,—that is, products which are generally obtained from starch by artificial processes. The ordinary starch can only be recognised by the iodine reaction after the extraction of the greater part of the dextrins. The other cereals cultivated in Japan also contain starch similar to that of the Mozi rice. The starch of the potato, and ordinary starch yield soluble starch, or at least a body coloured red by iodine, and also dextrin. The difference between all these varieties of starch is therefore quantitative not qualitative. The Mozi rice contains too little ordinary starch to form a paste, or to give a yellow colour with bromine. It contains no substance giving a violet colour with iodine as Nägeli supposes. J. M. H. M.

Absorption of Nitrogen by Soils and Plants. By A. GAUTIER and R. DROUIN (*Compt. rend.*, 106, 1605—1607).—A reply to Chevreul (this vol., p. 979).

Experimental Plots at the Agricultural Station of La Somme. By A. NANTIER (*Ann. Agronom.*, 14, 255—261).—*Wheat.*—Experiments were made with six well-known varieties of wheat at Senarpont on two very different soils, the one clayey and the other calcareous. In the rich clay, all gave good crops, Dattel and Bordeaux the best; in the light soil, Bordeaux was decidedly the best; in both soils, the Browick variety answered poorly. One result of these experiments is that the highly cultivated varieties need good, deep, rich, well-prepared soil. Various artificial manures were also tried with the Bordeaux wheat on the two soils already mentioned. The phosphatic manures were applied in the autumn, the soluble manures in the spring. The clay soil contained 0.207 per cent. N, 0.134 per cent. P_2O_5 , and 0.237 per cent. K_2O ; the calcareous soil, 0.202 per cent. N, 0.148 per cent. P_2O_5 , and 0.149 per cent. K_2O . Although these chemical features of the soils were so similar, the action of manures was very different in the two cases. None of the manures employed gave any increase in the calcareous soil, whilst on the clay soil sodium nitrate, ammonium sulphate, soluble and insoluble phosphate each gave an increase of about 10 quintals per hectare, the unmanured plot yielding 30 quintals. Potassium salts alone gave no appreciable increase, as might have been predicted. The soluble and insoluble phosphates were equally efficacious.

Irrigated Pastures.—Figures cited by the author show that a pasture which without irrigation gave 1500 kilos. hay per acre as first cut, and no aftermath, when irrigated gave 5000 and 6000 kilos. hay first cut, 2700 and 3500 kilos. second cut, total 7700 and 10,100 kilos.

Insoluble Phosphates.—These must be well worked into the soil in order to produce good results. Applied only on the surface of a pasture poor in phosphoric acid (0.149 per cent. P_2O_5) but rich in nitrogen (0.481 per cent.) and potash (0.138 per cent. K_2O), little or no effect was produced. J. M. H. M.

Richness and Density of Wheat. By A. PAGNOUL (*Ann. Agronom.*, **14**, 262—272).—The average composition is as follows:—Water, 14·3; albuminoids, 11·0; starch and dextrin, 70·5; fatty matters, 1·2; cellulose, 1·7; ash, 1·6. The water being always near 14·0, and the sum of the ash and cellulose 3 to 4, in order to arrive at the starch, dextrin, and fat, it suffices to add 17 to the albuminoids, and subtract the sum from 100. The albuminoids are very variable, and in order to correlate the variation in this constituent and in the phosphoric acid with the physical characters of the grain, the author has examined 70 samples of different countries, varieties, and methods of growth, and has embodied the results in an elaborate table, under the following heads, arranging the different samples in order of their richness in nitrogen:—

Water.—This varies from 10·00 to 16·88 per cent.; mean 14·1.

Albuminoids, in undried sample, 7·87 to 16·06 per cent.; mean 10·43.

Albuminoids, in dried sample, 9·13 to 17·87 per cent.; mean 12·14.

P₂O₅, in undried sample, 0·448 to 1·016 per cent.; mean 0·661.

P₂O₅, in dried sample, 0·533 to 1·154 per cent.; mean 0·769.

Number of grains in 10 grams, 162 to 404; mean 240.

Weight of 1 grain in milligrams, 24 to 61; mean 41.

Volume of 1 grain cubic millimetres, 18 to 46; mean 32.

He also gives the apparent and real densities of the undried grain and the real density of the dried grain (calculated).

The richness in nitrogen and the density generally increase together, but not in any constant ratio. The samples rich in nitrogen are usually rich in phosphoric acid also, but here again the relation is an irregular one. There is no constant relation between the size of the grains and their richness in nitrogen, but usually the small grained varieties are richer than the large ones. The richness in nitrogen appears to depend more on the mode of cultivation and meteorological conditions than on the variety; different samples of the same variety are found in all parts of the tables. The different coloured grains in the same sample differ much in composition; thus in a sample of Berques wheat, the white grains gave 10·22 per cent. of albuminoids (dry), and the red grains 13·87 per cent. Tropical wheats are not always the richest in albuminoids; two samples from Egypt were amongst the poorest, whilst the red wheat of Saint Pol (France) was one of the richest. The square-headed Porion wheat, from which large yields have been obtained, gave 11·87 per cent. of albuminoids in the dried sample, close on the average of the whole series.

J. M. H. M.

Application of Potassium Chloride to Sugar Beet on Heavy Soil. By A. PETERMANN (*Bied. Centr.*, 1888, 443—450).—The results of three years' experiments show that when potassium chloride is applied as a manure to sugar beet, in conjunction with nitre and superphosphate, an increase in total yield is produced in some cases, yet the absolute yield of sugar per hectare is reduced.

E. W. P.

Analytical Chemistry.

Spectroscopic Notices. By H. W. VOGEL (*Ber.*, 21, 2029—2032).

—*Coal-gas Volatiliser.*—A test-tube containing the substance under examination is fitted with a double-bored cork. Into the one cork a tube is fitted which passes nearly to the bottom, whilst into the second hole a tube is fitted bent twice at right angles, and drawn out at the upper end to a jet. Above the jet a tube 10 cm. long and 57 mm. wide is held by means of a wire in such a way that it can be pushed down over the jet or drawn up as required. Coal-gas is passed through the apparatus over the heated solution in the tube, and burns at the jet. The wide tube is so arranged that the flame is non-luminous. The apparatus can be used in most cases where the "hydrogen volatiliser" has hitherto been used, and is more convenient.

2. *Detection of Chromates.*—This is most readily effected by heating the substance in the apparatus just described with sodium chloride and sulphuric acid, when chromium oxychloride is formed if a chromate is present. A very characteristic spectrum is obtained, and 1 mgm. of a chromate can be detected.

3. *Observations of Deep Layers of Liquids in Test-tubes.*—The apparatus employed consists of a vertical spectroscope, a test-tube containing the liquid to be examined, and below this a mirror to reflect light through the liquid in the test-tube. In order to get over the inconvenience caused by the round bottom of the test-tube containing the liquid acting as a lens which focuses the light reflected into the tube to a point within the liquid, the test-tube is fitted into a larger test-tube which contains a little water, and thus forms a plano-convex lens. The outer tube being a fixture, the inner tube is pushed up or down until the greatest amount of light is obtained. With a depth of 16 cm., the chromous reaction can be observed when only 1.5 per thousand is present. Sketches of the apparatus are given.

N. H. M.

Funnel for Filtering Carbon. By T. M. DROWN (*Chem. News*, 57, 223).—This funnel has a cylindrical stem, of which the diameter is slightly less than the internal diameter of the porcelain combustion tube used. In use, the funnel is about half filled with asbestos, which is supported by a flat coil of platinum or copper wire, the end of which extends from the centre to below the end of the stem. When all the carbon is on the filter, the coil is withdrawn through the stem, and the funnel and contents dried. Now by inserting the stem in the combustion tube, the contents are easily and safely transferred. Successful determinations have been made by treating iron borings directly on the filter with cupric ammonium chloride solution, washing with dilute hydrochloric acid, &c., and burning without removal of the small amount of copper which may be present. Direct treatment in a glass combustion tube is not as satisfactory as using the funnel and transferring to a porcelain tube.

D. A. L.

Estimation of Bromine. By J. T. WHITE (*Chem. News*, **57**, 233—245).—Bromine is evolved when a bromide is heated with potassium permanganate and aluminium sulphate, whilst chlorides and iodides do not yield chlorine or iodine under these conditions. The author proposes a method of estimating bromine. The solution of a bromide is mixed with 10 c.c. of a permanganate solution (1 in 25) for each 0.1 gram bromine, and then with some aluminium sulphate solution saturated at ordinary temperatures; the bromine is distilled off in a current of carbonic anhydride and titrated.

D. A. L.

Determination of Phosphorus in Iron by Molybdate. By C. MEINEKE (*Zeit. angewand. Chem.*, **1**, 68—72).—The author cannot confirm Tamm's statement (this vol., p. 529) that the presence of manganese is prejudicial to the determination of phosphoric acid. He obtains identical results whether the iron is separated from the manganese as acetate, or whether the treatment is omitted. The amount of phosphoric acid precipitable after simple dissolution of the iron in nitric acid does not bear any constant proportion to that found after evaporation and ignition. Instead of the evaporation and ignition, the complete oxidation of the phosphorus can be effected by adding chromic acid to the nitric acid solution. With irons containing more than 3 per cent. of carbon, the addition of some sulphuric acid is necessary. The process is as follows:—4.375 grams of the iron are dissolved in 50 c.c. of nitric acid; 30 c.c. of diluted sulphuric acid (equal volumes of strong acid and water) is added, and the whole is evaporated to 15 or 20 c.c.; $2\frac{1}{2}$ or 3 grams of chromic acid is now added, the liquid boiled for 10 minutes and then diluted. If manganese peroxide separates, it must be reduced by hydrogen dioxide, but this generally introduces traces of phosphoric acid. The solution is now made up to 250 c.c., filtered, and 100 c.c., after partial neutralisation with ammonia and heating to 90° , is precipitated with molybdate. The precipitate after being washed, first with acidified ammonium nitrate, and then with cold water (see this vol., p. 194), is gently ignited. A gram corresponds to 1 per cent. of phosphorus in the iron.

The organic matters in bog-iron ore are without influence on the determination of the phosphorus it contains.

M. J. S.

Determination of Alkaline Hydroxides in Presence of Carbonates. By A. ISBERT and VENATOR (*Zeit. angewand. Chem.*, **1**, 109—110).—The perfectly cold solution of the mixture is titrated with standard acid, using as indicator the special rosolic acid prepared as described in *Zeit. anal. Chem.*, 1887, 583. The change to yellow is perfectly distinct and sharp as soon as the hydroxide is neutralised. On now boiling the liquid, the red colour is restored, and a further quantity of acid, corresponding with the carbonate present, is required to produce the change to yellow.

M. J. S.

Volumetric Estimation of Potassium and Sodium. By J. T. WHITE (*Chem. News*, **57**, 214—215).—21 c.c. of the solution containing about 0.2 gram of the mixed chlorides is placed in a 100 c.c.

flask, and for each 0.1 gram of the mixed salts 5 c.c. of a solution of ammonium hydrogen tartrate is added. This solution is prepared by diluting a solution of ammonium hydrogen tartrate saturated at 90° with an equal volume of water, and warming before use to dissolve any crystals. When the flask and contents are cool, methylated spirit is added gradually, shaking after each addition until the flask is filled to the mark; after three hours or longer, the potassium hydrogen tartrate is filtered off, and 10 c.c. of the solution evaporated to dryness, ignited, then again evaporated with ammonium chloride solution, and re-ignited. The residual sodium chloride is titrated with silver nitrate.

D. A. L.

Solubility of Magnesium Ammonium Phosphate in Alcohol.

By A. J. WAKEMANN (*Technology Quarterly*, Boston, 1, 173—177).—The author mentions that Rose, in the sixth edition of his *Handbuch der Analytischen Chemie*, points out that the precipitate of magnesium ammonium phosphate is entirely insoluble in water containing one-fourth of its bulk of ammonia solution of specific gravity 0.96°, and that under the determination of phosphoric acid by magnesium salts, Rose states that water containing 3 per cent. of ammonia gas dissolves only traces of the precipitate, and that this solubility is reduced to less than half if to the dilute solution of ammonia one-fourth of its volume of alcohol is added, and, further, that the addition of alcohol favours the separation of the precipitate.

The author, in order to test the method, which he says appears to have been neglected by analysts, has made a series of comparative analyses under identical conditions with the exception that some of the precipitates were washed with ammonia solution, according to the ordinary method, and the remainder with ammonia solution containing alcohol.

The results of his experiments point to a slight advantage in the use of alcohol in diminishing the solubility of magnesium ammonium phosphate when the precipitate is somewhat bulky. The use of alcohol, moreover, appears to make the precipitate more compact, so that it is more easily washed, and is less liable to creep up the sides of the funnel. The addition of alcohol to the solution in which the precipitation takes place is not advantageous, as it causes the precipitate to attach itself more closely to the beaker, so as to be difficult of removal, and it also retards the filtration.

G. W. T.

Solvent Action of Rochelle Salt on Metallic Hydroxides.

By H. N. WARREN (*Chem. News*, 57, 223—224).—The author includes the moist precipitates of the following metals in the list of hydroxides and carbonates soluble in solutions of Rochelle salt:—Copper, zinc, manganese, nickel, cobalt, iron (ferrous and ferric), chromium, aluminium, tin (stannic), antimony, bismuth, and even barium, strontium, calcium, and magnesium to a considerable extent in concentrated solutions of Rochelle salt. Cadmium carbonate is, however, insoluble. Treatment with Rochelle salt solution cannot, therefore, be safely employed for distinguishing or separating bismuth or tin from antimony, although it is frequently recommended for that purpose.

Cadmium carbonate may, however, be separated from copper carbonate by such treatment. D. A. L.

Determination of Manganese as Sulphide. By C. MEINEKE (*Zeit. angewand. Chem.*, **1**, 3—5).—Manganese sulphide when thrown down in the green form can be easily washed by decantation, and shows no tendency to pass through the filter. The green modification is readily obtained by precipitating from a boiling solution containing a large excess of ammonia. After boiling for a few minutes and allowing to subside, filtration may take place immediately. A trace of manganese remains in solution, but not more than after precipitation in the cold. It may be recovered, if desirable, by evaporating to a small bulk, acidifying, filtering from sulphur, and precipitating with bromine and ammonia. Traces also adhere to the precipitation vessel, and should be dissolved with hydrochloric acid containing bromine. The results are not influenced by the presence of large quantities of ammonium chloride or acetate, or of sodium chloride, or by dilution. Satisfactory results have been obtained in the separation of manganese, calcium, and magnesium. For weighing, the precipitate is best converted into Mn_2O_3 , for which purpose ignition at a bright-red heat, with exposure to air until the weight is constant, suffices. M. J. S.

Determination of Small Quantities of Manganese in Iron rich in Silicon. By C. REINHARDT (*Zeit. angewand. Chem.*, **1**, 108—109).—Hampe's chlorate process (*Abstr.*, 1886, 101) is unsuitable for such irons owing to the large quantity of gelatinous silica which separates during the solution in nitric acid. The following modification of Belani's method can be employed:—3 or 4 grams of the iron is covered with 30 or 40 c.c. of hydrochloric acid (1.19); some potassium chlorate is added, and after standing for some time in the cold the solution is heated and evaporated to 15 or 20 c.c. It is then diluted with cold water and filtered through a Schleicher's filter into a 500 c.c. flask, washing the silica with hot water. For each gram of iron, 5 c.c. of nitric acid (1.4) is now added. The solution is boiled, cooled, neutralised with zinc oxide until the ferric hydrate is precipitated, then made up, mixed, and filtered. Half of the filtrate is boiled with sodium acetate, bromine, and zinc oxide, and the precipitated peroxide is titrated with oxalic acid and permanganate. M. J. S.

Determination of Iron by Nitroso- β -naphthol. By C. MEINEKE (*Zeit. angewand. Chem.*, **1**, 5—7).—The method described differs little from that of Ilinski and Knorre (*Abstr.*, 1886, 100). The solution must not contain nitrates. It is desirable, although not necessary, that the iron should be in the ferric state. The solution should be as nearly neutral as possible. About 1 gram of nitroso- β -naphthol dissolved in 2 c.c. of 50 per cent. acetic acid is required for each decigram of iron. The precipitation is best performed in the cold. It is complete when a drop of the clear upper liquor gives a brown colour with a cobalt solution. The precipitate after having been washed with cold water, is so far dried that the rim of the filter can be

wrapped round it, and it is then very gradually heated in a large porcelain crucible until completely burnt to ferric oxide.

Cobalt and copper if present are precipitated along with the iron. Phosphoric acid appears sometimes to be completely and at other times imperfectly thrown down. M. J. S.

Determination of Alcohol. By B. RÖSE (*Zeit. angewand. Chem.*, 1, 31—35).—An excess of potassium permanganate oxidises alcohol completely to carbonic acid and water when to the mixture so much concentrated sulphuric acid is added that it amounts to 40 per cent. of the whole. The author's experiments were made with absolute alcohol distilled from quicklime in an apparatus from which moist air was excluded. It boiled at 78.26° (corr.). From this, a 1 per cent. solution was made with purified water. The permanganate solution contained 10 grams in a litre, and was standardised by potassium quadroxalate, a decinormal solution of which is also required. The analytical process is as follows:—About 5 grams of the dilute alcohol is weighed in a flask; 50 c.c. of the permanganate is run in, and then 20 c.c. of sulphuric acid whilst shaking. After a few minutes, 100 c.c. of water is added, then a measured excess of the oxalate, the liquid heated nearly to boiling, and the excess of the oxalate found by permanganate. In four experiments, 100.18, 100.0, 100.24, and 100.0 per cent. of the alcohol present was indicated. M. J. S.

Estimation of Glycerol. By F. FILSINGER (*Zeit. angewand. Chem.*, 1, 123—124).—The substitution, proposed by Jolles, of potassium manganate for permanganate in the Benedict-Zsigmondy process (which is based on the oxidation of the glycerol in cold alkaline solution to oxalic acid and titration of the latter after precipitation by calcium chloride) is found to yield low and irregular results even when a large excess of manganate is employed. M. J. S.

Influence of Inactive Substances on the Polaristrobometric Estimation of Grape-sugar. By R. PRIBRAM (*Monatsh.*, 9, 395—405).—The rotatory power of solutions of grape-sugar containing acetone increases with the percentage of acetone, so that $[\alpha]_D = 16.587 + 0.026x$ where $[\alpha]_D$ is the rotation at 20° ($l = 2dm$), 16.587 is the rotation of the sugar alone in solutions containing 15.68 grams in 100 c.c., and x is the percentage of acetone. The rotatory power of sugar solutions containing acetone reaches its maximum only after a certain lapse of time, and the viscosity of such solutions increases with the percentage of acetone. These facts must be borne in mind in estimating the sugar in diabetic urine when more than 5 per cent. of sugar and 1 per cent. of acetone are present; smaller quantities have quite inappreciable influence on the results.

The rotatory power of tartaric acid is considerably diminished in the presence of acetone.

Carbamide lowers the rotatory power of grape-sugar, but only slightly; ammonium salts act similarly but to a larger extent.

8 to 10 per cent. of phosphates lowers the rotatory power slightly, smaller quantities have no appreciable effect. F. S. K.

Determination of Starch in Grain. By MONHEIM (*Zeit. angewand. Chem.*, 1, 65—68).—The direct inversion of the starch with hydrochloric acid gives results which are too high, owing to the conversion of the cellulose into sugar (Märker, *Handb. d. Spiritusfabr.*, 4th Ed., 93). Asboth's method (Abstr., 1887, 868) gives most unsatisfactory results, concordant numbers being obtained only when the same baryta solution is used, and the results being even then in many cases incredible. The author gives the preference to Lintner's method. 3 grams of the ground grain with 50 c.c. of water are heated for four hours in a pressure bottle in a paraffin-bath at 135—140°. The solution is filtered, and after dilution to 200 c.c. is inverted by adding 20 c.c. of hydrochloric acid and heating for three hours on the water-bath in a flask with inverted condenser. The solution is neutralised, filtered, made up to 500 c.c., and titrated by Fehling's solution. The sugar found, multiplied by 0.916, gives the amount of starch. The use of lead acetate for decolorising the solution introduces errors. The best mode of making the titration is to measure out, dilute, and heat the copper solution, then add at once a certain quantity of the sugar solution, boil for two minutes, and examine the upper liquor. If too much or too little of the sugar has been used, a fresh quantity of the copper solution should be taken. The use of potassium ferrocyanide as indicator is altogether misleading.

M. J. S.

Determination of Starch by Baryta. By F. SEYFERT (*Zeit. angewand. Chem.*, 1, 126—129).—Asboth's method (Abstr., 1887, 868) is capable of giving results agreeing very closely amongst themselves when the conditions are kept precisely similar. A very important point is the strength and quantity of the alcohol used, the limits being comparatively narrow within which the amount of baryta precipitated is such as to correspond with the formula given by Asboth. The use of 50 c.c. of 45 per cent. alcohol in making up the mixture to 250 c.c. gives results nearest the truth. The starch must be very thoroughly gelatinised, one to two hours on the water-bath being necessary. The baryta solution should not contain less than 23 grams of barium oxide in the litre.

M. J. S.

New Extraction Apparatus. By C. M. KING (*Chem. News*, 57, 235—236).—This apparatus consist of a wide test-tube, *a*, with a quill tube *b* fused into the bottom and extending some way both inside and beyond *a*. The end of *b* inside *a* is cut off obliquely, and upon its apex rests the closed end of a slightly wider tube *c*, which reaches nearly to the bottom of *a*. *a* is inclosed in a still wider tube *d*, and is supported on small projections just above the narrower lower end of *d* into which the quill *b* tube extends from the bottom of the test-tube *a*. In operation, the substance to be extracted is placed in the space between the test-tube *a* and the tube *c*, and rests on a plug of glass-wool attached to the tube *c* in such a way as to leave a clear, liquid space below. The upper part of the tube

d is connected with a condenser, whilst the narrow part passes through the cork of the flask containing the solvent; as distillation proceeds, the test-tube *a* and the space between the tubes *b* and *c* gradually fill up until the open end of *b* is reached, when the extract syphons off into the flask below; in this manner the solvent continues to circulate until the operation is complete. D. A. L.

Determination of Fat in Milk. By B. RÖSE (*Zeit. angewand. Chem.*, **1**, 100—107).—About 20 grams of the milk is mixed with 2 c.c. of ammonia, then 45 c.c. of alcohol, and 120 c.c. of a mixture of equal parts of ether and light petroleum, and is shaken in a stoppered burette of 230 c.c. capacity. The volume of the ethereal layer is read off and 25 c.c. of it is evaporated in a tared flask, the fat being dried by aspirating dried air through the flask for 10 minutes, whilst heating in a glycerol-bath at 90°. An addition of 0.015 per cent. should be made for fat remaining in the aqueous layer.

When milk is evaporated with sand, the fat must be extracted the same day; if the dry residue is kept, the amount of fat obtainable from it diminishes very seriously (see next Abstract). M. J. S.

Determination of Fat in Milk. By H. SCHREIB (*Zeit. angewand. Chem.*, **1**, 135).—In the course of a considerable experience of the sand process for determining fat in milk, the author has not encountered results confirming the statement of Röse (preceding Abstract), that the dry residue if preserved for several days before extraction with ether yields less fat than if extracted at once. In special experiments made for the purpose, the same amount of fat was obtained by extracting on the fourth day as on the first, and that whether the residue were preserved in paper (as in Röse's experiments) or in the basins in which the evaporation took place.

M. J. S.

Adulteration of Butter. By P. BOCKAIRY (*Bull. Soc. Chim.*, **49**, 247—251, and 331—335).—15 c.c. of the dry, melted and filtered butter are poured into 15 c.c. of toluene, placed in a graduated tube, and 40 c.c. of alcohol (96.7° Gay-Lussac) added; at 18° the toluene, containing the fat in solution, remains at the bottom of the vessel. The tube is then placed in water at 50°, and the mixture agitated, after which it is placed in water at 40° for half an hour. In the case of pure butter no precipitate, or only a slight cloud, is formed; if, however, extraneous fats are present, an oily or flocculent precipitate deposits, from the quantity and character of which the amount and nature of the adulteration can be roughly estimated.

The results obtained with pure butter from various sources, and with the same butter after the addition of varying quantities of fats, are given in tabular form. If 2 to 3 c.c. of precipitate are obtained, the butter is most probably adulterated, but when the precipitate exceeds this volume the sample is certainly impure. 10 per cent. of added oleomargarine, margarine, olive oil, beef-fat, &c., causes a precipitate of from 10 to 12 c.c.; 75 per cent. of the same impurities produce

a precipitate of from 19 to 22 c.c., intermediate quantities give proportional precipitates.
F. S. K.

Detection of Cotton-seed Oil in Olive Oil. By F. JEAN (*Dingl. polyt. J.*, **268**, 101).—The author has obtained good results with Becchi's method, which requires the following solutions:—(1) 1 gram of silver nitrate dissolved in 100 c.c. each of alcohol and ether, (2) 85 parts of amyl alcohol (boiling at 130—132°), and 15 parts of pure rape oil. 10 c.c. of the oil to be examined is mixed in a glass tube with 11 c.c. of the silver solution and 8 to 10 c.c. of the rape oil solution. The mixture is then heated for 15 minutes in a water-bath. If cotton-seed oil is present, a brown coloration is obtained.
D. B.

Detection of Sesame Oil in Cocoa-butter. By P. ZIPPERER (*Chem. Zeit.*, **11**, 1600).—Sesame oil is frequently added in small quantities to chocolate to give it a glossy surface and good fracture. When such chocolate is extracted for analysis, the sesame oil is dissolved along with the cocoa-butter. It may be detected by gently warming 2 c.c. of the suspected cocoa-butter with a freshly prepared mixture consisting of 1 c.c. hydrochloric acid, sp. gr. 1.18, and 0.05—0.1 gram of cane-sugar; the production of a raspberry-red coloration indicates the presence of sesame oil; pure cocoa-butter under similar circumstances gives a yellowish to dark-brown colour. In this manner, an admixture of $\frac{1}{50}$ per cent. of sesame oil may be detected.
D. A. L.

Detection of Acetanilide. By D. VITALI (*Chem. Centr.*, 1888, 424, from *L'Orosi*, **11**, 1—5). Acetanilide (antifebrin) could not be detected in the urine of people who had consumed this compound. The following method was used: the urine, either in its original state or neutralised with ammonia, was extracted with five times its volume of ether. The ethereal solution gave no residue. Acetanilide gives the following colour reactions. A trace of it gives a blue coloration with a few drops of a solution of bleaching powder and a crystal of phenol. Mixed with a solution of potassium chlorate in sulphuric acid, it produces a red colour, which is changed to yellow by water, by heating to blood-red. With a crystal of potassium nitrite and a drop of concentrated hydrochloric acid, acetanilide produces a yellow colour, which, on heating, changes through green to blue. On evaporation to dryness, an orange-coloured residue remains, which is coloured red by ammonia.
J. W. L.

Detection of Pyridine Bases. By WEPPE and LÜDERS (*Chem. Zeit.*, **12**, 151).—Cadmium chloride has been employed for the detection of pyridine in denaturated spirit; a 5 per cent. solution of the salt should produce a decided turbidity in a few seconds, in an aqueous solutions of 1 of base in 250 of water. Many operators have failed to obtain this reaction, and the authors now show that this is very probably due to variations in the composition of the cadmium chloride. In two samples of this salt, one giving the reaction contained more

cadmium than the other which did not produce the turbidity. The test is uncertain therefore. D. A. L.

Estimation of Morphine in Opium. By E. F. TESCHEMACHER and J. D. SMITH (*Chem. News*, 57, 244—245).—A controversial communication referring to R. William's paper (*loc. cit.*, 134—135, and this vol., p. 635). Incidentally it is noted that all they "pretend to do" by their method "is to return results certifying to the amount of pure crystalline morphine which can be obtained from a given sample of opium," and moreover they assert that they obtain more morphine than any other analysts do; but do not place implicit reliance on their method, nor do they believe in its giving accurate results. D. A. L.

Delicate Test for Morphine. By J. L. ARMITAGE (*Phil. J. Trans.*, 18, 761).—When ferric chloride is added to a solution of a morphine salt, a bluish-green coloration (imperceptible in dilute solutions) occurs due to the reduction of some of the ferric chloride to the ferrous state, and when potassium ferricyanide is added, a deep-blue coloration takes place, or in very dilute solutions, a greenish-blue coloration. One part of morphine salt in 100,000 will give this reaction unmistakably after standing a few minutes. This is a delicate confirmatory test in the absence of other reducing substances which would give the same reaction, but several other alkaloids submitted to this test failed to give the coloration. R. R.

Difference between the Colouring Matters of Bilberry and Wine: Spectroscopic Wine Testing. By H. W. VOGEL (*Ber.*, 21, 1746—1753).—The fresh colouring matters of bilberries and wine are similar but not identical. They are readily distinguished from one another by their absorption-spectra after they have been carefully neutralised with ammonia, or better still when they are treated with a trace of a solution of alum before neutralising with ammonia. The unsuccessful results obtained by others are attributed to the use of too concentrated wines and the addition of too much ammonia. When fermented or when kept long, the colouring matters can no longer be distinguished from each other. The positions of the absorption-bands in each case are shown in a table. (Compare Andree, *Arch. Pharm.*, 13, 90.) N. H. M.

Testing for Santonin. By L. KNAPP (*Dingl. polyt. J.*, 268, 42—44).—In the process of extraction and purification of santonin, solutions and extracts are obtained which may contain santonin and therefore require to be tested for the presence of this substance. Linde's reaction consists in mixing a few drops of the solution with concentrated sulphuric acid, whereby a violet colour is obtained varying in depth of tint with the amount of santonin present in the solution. This test can, however, be applied only to colourless solutions. In order to examine coloured solutions, Kossakoffsky recommends precipitating the colouring matter with lead acetate and then treating the filtrate with sulphuric acid. D. B.

The Vienna Gravimetric Method of Estimating Tannin in Concentrated Solutions.—By R. KOCH (*Dingl. polyt. J.*, 268, 329—334).—The author refers to the publication of the results of some analyses made by Simand, which show that the amount of extract and the percentage of tannin are not influenced by the quantity of bark operated on. The same chemist also asserts that with extracts of different concentrations the same amounts of soluble and insoluble tannin are obtained. As these conclusions are in opposition to Counciler's results and disagree with the author's experience of the Vienna method, the following experiments were carried out:—

60 grams of fir bark was extracted by means of the Vienna extraction apparatus and the concentrated solution diluted to 1 litre. It was then again heated in order to redissolve any precipitated tannin, after which it was allowed to cool to 18°.

Experiment 1.—50 c.c. of this solution was evaporated to dryness on a water-bath. The residue weighed 0.870 gram, equal to 29 per cent.

Experiment 2.—50 c.c. was diluted to 150 c.c., warmed, allowed to cool to 18°, filtered, and 50 c.c. of the filtrate evaporated to dryness and weighed. The residue gave 0.274 gram = 27.4 per cent.

Experiment 3.—50 c.c. of the concentrated solution yielded on evaporation 0.736 gram of residue, corresponding to 24.52 per cent. of solid matter.

Experiment 4.—50 c.c. of the concentrated solution was filtered, diluted with three times the volume of water, and 50 c.c. of this evaporated to dryness. The residue weighed 0.245 gram = 24.5 per cent.

From these results the author draws the conclusion that different amounts of soluble tannin are obtained, when 20 or 60 grams of bark are extracted with one litre of water. Similar results were obtained with extracts of quebracho bark subjected to the above treatment in a solid and pasty form. The author recommends therefore for the estimation of the soluble tannin, the use of a small quantity of bark and a considerable amount of water, whilst for the solids other than tannin it is best to employ for extraction a large quantity of bark.

D. B.

Estimation of Tannin. By C. COLLIN and L. BENOIST (*Chem. News*, 57, 214).—In the process recommended, the following solutions and apparatus are required. A normal solution of tannin containing 5 grams of pure dry tannin and 0.5 c.c. of a solution of mercuric iodide (1 in 10, the iodide being dissolved by means of an equal weight of iodide of potassium) in a litre of water. A standard solution of gelatin, containing 5 grams of gelatin dissolved in a litre of water; it is clarified with egg albumin, mixed with 0.5 c.c. of the mercuric iodide solution and made slightly alkaline with soda. A calcium acetate solution containing 50 grams of the salt dissolved in a litre of water, which is filtered and a few drops of mercuric iodide solution are added. The mercuric iodide is intended to prevent fermentation or fungoid growths. Besides these a 1 per cent. solution of methylene blue, a 4 per cent. solution of Nicolson blue, and a 1 per cent. solution of black blue, "N.B.I.," for use with coloured tannins and

extracts must be at hand. The apparatus consists of a burette to read to $\frac{1}{100}$ ths of c.c. delivering 4 drops to a tenth c.c., and a stoppered test-tube 3 cm. in diameter, and marked at 60 c.c. The gelatin is standardised by taking 1 c.c. of the solution in the test-tube, adding two drops of methylene-blue and 5 c.c. of calcium acetate solution, filling up to the mark with water at 75° to 80°. The quantity of tannin required to precipitate this gelatin is then ascertained by running in normal tannin solution a little at a time, agitating after each addition, until the solution is colourless. The quantity of tannin in any solution may then be determined by employing it instead of the normal solution for the precipitation of the gelatin. Strong tannin solutions should be diluted before titration.

D. A. L.

Spectroscopic Examination of Blood. By G. LINOSSIER (*Bull. Soc. Chim.*, 49, 691—694).—Contrary to the opinion almost universally held, it is not the absorption-bands of oxyhæmoglobin which give the most sensitive spectroscopic reaction, but those of reduced hæmatin (the hæmochromogen of Hoppe-Seyler). The author recommends the following method for the spectroscopic examination of blood:—The blood-stain is dissolved in water with the usual precautions and examined for the spectrum of oxyhæmoglobin. A drop of a freshly prepared solution of sodium hyposulphite is then added; the spectrum of reduced hæmoglobin instantly appears. Finally, one or two drops of a concentrated solution of soda are added; the hæmoglobin is thus decomposed into globulin and reduced hæmatin, the spectrum of which consists of two bands. The more intense band is the only one which can be distinctly observed when the solution of blood is very dilute; it is situated at an equal distance from the D and E lines, and occupies the luminous region which separates the two bands of oxyhæmoglobin; its mean position corresponds with that of the ray whose wave-length is $\lambda = 557$. The second band is more diffuse, and is situated between the lines E and B, its mean position corresponds with $\lambda = 522$. A slight elevation of temperature favours the appearance of this spectrum which, if the solution is very dilute, may only manifest itself after the liquid has been completely cooled.

The last experiment gives positive results only when the solution of blood is extremely dilute, and it is advisable, therefore, to make sure that the spectrum observed is really that of hæmatin. This can be done by the following tests:—The band ought to disappear if the liquid is heated to 50° without agitating, and reappear on cooling. The band ought to disappear when the solution is agitated in the air, and reappear when a drop of sodium hyposulphite is added. If the colouring matter has been radically changed by putrefaction, the spectroscopic reaction of reduced hæmatin may be the only test by which the presence of blood can be proved. In some cases, the colouring matter has become insoluble in water; the stain is then dissolved in tolerably strong ammonia, and the oxyhæmatin is best reduced by one or two drops of a solution of ferrous sulphate and tartaric acid. The spectrum of such a solution shows clearly the first band of the reduced hæmatin.

By this method of spectroscopic examination, blood can often be detected in cases where crystals of hæmin cannot be obtained.

F. S. K.

Detection of Blood Stains. By FERRY DE LA BELLONE (*J. Pharm.* [5], 17, 253—255, from *Rép. de Pharm.*).—If the stains are on linen or cloth, some filaments of the fabric are placed on the surface of a solution of sodium chloride, 1 : 1000, in a small glass tube; after some hours the liquid takes a brownish-rose tint. If spectroscopic examination of the liquid indicates hæmoglobin, the search for blood corpuscles becomes important. A drop or two of concentrated chloral solution is added to the liquid, when a rose-coloured precipitate is quickly deposited. The supernatant liquid is removed by means of a pipette, a drop of the deposit is spread out on a glass slide, and carefully warmed over a lamp; a reddish coagulum is formed, and a clear liquid which is removed by filter-paper. The coagulum is stained with a little magenta, washed, and to it is added a drop of dilute acetic acid. The globules stained a bright-red are then visible under the microscope. When the stain is found on instruments, wood or stone, &c., the powder obtained by scraping is placed in a fine bag and suspended in the salt solution. When the powder is mixed with earth, the clay usually present causes a rapid precipitation in the salt solution; in this case, the reddish particles should be picked out, under the microscope, for testing. In all cases, the results may be confirmed by the formation of hæmin crystals. For this purpose, one or more drops of the brown-rose solution is taken before the addition of chloral, and carefully evaporated to dryness on a slide. It is then covered and warmed with a drop of glacial acetic acid when the crystals of hæmin appear in large numbers on cooling.
J. T.

Detection of Albumin, Propeptone, and Peptone. By C. POSNER (*Zeit. anal. Chem.*, 27, 408—409, from *Arch. Physiol.*, 1887, 495).—The liquid (urine, &c.), is rendered alkaline and a solution of copper sulphate so dilute as to be nearly colourless is poured on its surface. Peptone in the cold, or albumin after heating, gives a reddish-violet ring at the point of contact.
M. J. S.

General and Physical Chemistry.

Relations between the Composition and the Absorption-spectrum of Organic Compounds. By G. KRÜSS (*Zeit. physikal. Chem.*, **2**, 312—337).—The absorption-spectra of solutions of derivatives of indigo, fluorescein, and anthracene were examined, the solvents being chloroform or concentrated sulphuric acid for the indigo and anthracene, and alcohol or water for the fluorescein-derivatives. The wave-lengths of the lines of maximum absorption are given for every compound, the number of compounds examined being in all 64. From these observations, and those of others, the author finds generally that the substitution of a methyl-, ethyl-, methoxyl-, or carboxyl-group, or of bromine for hydrogen, moves the absorption lines further towards the red, and that the substitution of a nitro- or amido-group causes a movement further towards the violet. The only exceptions found were for dibromamido-indigo and bromalizarin in the first case, and for the alcoholic solutions of tetranitro- and dibromodinitro-fluorescein in the second, the behaviour of these being directly opposite to the normal one. The aqueous solutions of the last two compounds follow the general rule. The displacement caused by the introduction of any of the above groups appears to depend in amount on the nature of the compound into which the group enters, but general rules for this cannot be deduced.

If the production of absorption lines be looked on as caused by absorption, by a compound, of those ether waves which are capable of vibrating in unison with its own molecules, then the number of vibrations of such molecules would be given by $n = v/\lambda$, v being the velocity of light, λ the wave-length corresponding with the absorption line. Increase of λ by movement of the line towards the red would mean a decrease in n , and decrease of λ by movement towards the violet, an increase of n . From this it would appear that the introduction of methyl, ethyl, methoxyl, carboxyl, or bromine into a molecule, in place of hydrogen, retards; the introduction of a nitro- or amido-group, accelerates its vibrations. H. C.

Cause of the Change of Specific Rotatory Power under the Influence of Various Solvents. By G. J. W. BREMER (*Rec. Trav. Chim.*, **6**, 255—261).—A reply to Příbram (*Abstr.*, 1887, 755), in which the author endeavours to show that Příbram's results do not prove conclusively that the specific rotatory power of a solution continually decreases as it is more and more dilute. F. S. K.

Reactions in Secondary Coils (Elements). By LODSINSKY (*J. Russ. Chem. Soc.*, 1887, 542—548).—The author recapitulates the results obtained by Gladstone and Tribe, Frankland, Aron, Tcheltoff, Beklemisheff, and Kanin, and shows that it is necessary to investigate

exactly the dependence of charge, quantity of electricity, and E.M.F. on the concentration of the sulphuric acid used. It is first shown by quantitative experiments that the reaction really consists in the formation of a sulphate: $\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_{4,\text{aq}} = 2\text{PbSO}_4 + 2\text{H}_2\text{O} + \text{aq}$. The reverse action is shown to take place on charging the elements, so that Aron's hypothesis that hydrated peroxide of lead is formed is erroneous. It is shown further that Frankland is right in recommending to charge the batteries in intervals, for time must be given for the exchange by diffusion of the weaker acid formed inside the plates with the stronger acid outside, otherwise formation of PbO alone, but no sulphate, would take place, and the energy of the reaction $\text{PbO} + \text{H}_2\text{SO}_{4,\text{aq}}$ would be lost. From the absence of sulphuric acid in the plates, the formation of PbO_2 is explained, as otherwise the PbO first formed would become converted at once into the sulphate. It is shown by quantitative experiments that owing to slow diffusion, the concentration of the acid becomes greater than it was at the commencement of the experiment, both on discharging as well as on charging.

B. B.

Theory of the Dissociation of Electrolytes. By W. OSTWALD (*Zeit. physikal. Chem.*, 2, 270—284).—Various considerations are advanced in support of Arrhenius' theory of the dissociation of electrolytes. The difficulty in recognising dissociation among salts which are looked on as chemically very stable, lies in the confusion of the affinity with which the elements are combined in such compounds, with that which appears active in the behaviour of these compounds towards others. The two are not of the same but of opposite properties. The more energetic a substance is chemically, the easier will it be split up into its atoms; and the greater the power with which its elements are held together, the less will be its chemical activity. The existence of atoms of such elements as potassium and sodium in water can be understood when it is remembered that their condition as ions with large electric charges is very different from that of the same atoms in the so-called free state.

The author has shown, from the action of acids, that certain so-called coefficients of affinity may be deduced for these, which are independent of the nature of the chemical reaction from which the coefficients are obtained, and are proportional to the electrical conductivities. These affinity coefficients would, in the light of the present theory, represent nothing more than a measure of the dissociation of the acids. For the greater the extent to which dissociation into hydrogen and free ion had already taken place, the more readily would the combination of either of these two with other groups take place. And since the dissociation is independent in amount of the nature of the reaction into which the acid enters, this would explain how for the same acid the same coefficient of affinity is obtained in every reaction.

The equation $(\mu_\infty - \mu_v)\mu_\infty v/\mu_v^2 = c$, which the author has deduced from the dissociation theory (this vol., p. 1020), expresses the whole electrical behaviour of binary electrolytes. Thus as v increases, μ_v must also increase until at length it reaches the limiting value μ_∞ ,

which is the law of the increase of the molecular conductivity with increasing dilution. μ_{∞} is the conductivity of the wholly dissociated electrolyte, and since in this the motion of each ion is independent of that of the other, μ_{∞} should be deduced simply from the sum of these motions, and as a matter of fact μ_{∞} may be represented as the sum of two numbers, one of which depends on the nature of the negative and the other on that of the positive ion. This is only true for infinite dilution, for with greater concentration the law is merely approximate, owing to the dissociation not being complete. With acids and bases of low conductivity, μ_v is small in comparison with μ_{∞} , and $\mu_{\infty} - \mu_v$ becomes nearly constant, so that $\mu_v^2 = v \text{ const.}$ This is the law already established, that where the conductivity is low, it increases with rising dilution in proportion to the square root of the volume. If the dilutions v_1, v_2, \dots be measured at which electrolytes have the same relative conductivity, that is where the relation between μ_v and μ_{∞} is the same for all, then $\mu_{\infty}(\mu_{\infty} - \mu_v)/\mu_v^2$ will be constant, and $v_1/c_1 = v_2/c_2 = v_3/c_3 = \dots$, or the above dilutions stand in a constant relation, depending only on the nature of the electrolytes. The increase in the conductivity of all monobasic acids or monacid bases follows then the same law, which has been already established.

If $m = \mu_v/\mu_{\infty}$, we have $m^2/(1 - m)v = C$. This relation has been tested with various substances, and found to hold good with remarkable accuracy for both weak and strong acids from $m = 0.7$ to $m = 76$. Above this limit, the experimental errors have too great an influence to allow of its being tested. The effect of increasing the concentration of the solution also is to decrease the constant slightly. This is owing to the change in the molecular volume and in the viscosity, and if corrections for both be applied, the constancy becomes more apparent, even up to 10 per cent. concentrations. H. C.

Raoult's Law of Freezing. By W. HENTSCHEL (*Zeit. physikal. Chem.*, 2, 306—311).—The author describes a new form of apparatus for the determination of the freezing point. Experiments were made with various substances in benzene and acetic acid solutions, which tend on the whole to confirm the truth of the law. The numbers for acetic and formic acids in benzene show that they are present as double molecules, but benzene in acetic acid gives the normal value for a single molecule. The exception shown by acetic and formic acids leads the author to doubt the general validity of Raoult's law. The substance prepared by passing chlorine through a mixture of methyl formate and chloroformate (*J. pr. Chem.*, 36, 468; Abstr., 1888, 249) gave a molecular weight $\frac{1}{2}C_4H_5Cl_2O_4$, and from this and former investigations would appear to be a mixture of chloromethyl and dichloromethyl chloroformate in molecular proportion.

H. C.

Theory of Liquids. By G. P. GRIMALDI (*Zeit. physikal. Chem.*, 2, 374—377).—In criticism of Konowaloff's paper (this vol., p. 1019), the author shows that his own equation for the expansion $v_t = v_0/(1 - k_1t - k_2t^2)$ gives values for the coefficients of expansion which bring the calculated numbers for ϕ in the case of ether and

pentane into a closer agreement with the observed values than was obtained by Konowaloff. H. C.

Hypothesis of the Dissociation of Salts in very Dilute Solutions. By M. PLANCK (*Zeit. physikal. Chem.*, **2**, 343).—In answer to Wiedemann (this vol., p. 1021), the author points out that the value of E in the equation $E = \text{const. } n_1/n$ is not altered by a change in n . For the constant has the value θ^2/q , where θ is the temperature and q the latent heat of freezing; q combines in the denominator with n to the product nq , and this number, which is the latent heat of fusion of the whole solvent, depends directly on the weight and not on the size of the molecules of the latter. The author has further shown (*Ann. Phys. Chem.* [2], **34**, 149) that equilibrium in a solution of infinite dilution is independent of any polymerisation of the solvent, although not absolutely so in moderately dilute solutions. H. C.

Theory of Isohydric Solutions. By S. ARRHENIUS (*Zeit. physikal. Chem.*, **2**, 284—295).—An extension of the author's dissociation theory. Two solutions are isohydric, the electrical conductivities, or in other words the electrolytic dissociation of which remains unchanged when they are mixed. Let there be two acids, H_mA and H_nB , dissolved in water so that the volumes of the solutions are V_a and V_b . Further, let a molecules of the first remain undissociated, and α molecules be dissociated into the ions mH and A , and let b and β be the corresponding numbers for the second. Then if the solutions are isohydric, from considerations based on Van't Hoff's assumption of the analogy of the condition of salts in dilute solutions to the same in the gaseous state, we get $(m\alpha + n\beta)/(V_a + V_b) = m\alpha/V_a = n\beta/V_b$. These relations give expression to conditions which the author has already shown to exist in isohydric solutions (*Ann. Phys. Chem.* [2], **30**, 54; Abstr., 1887, 415).

The theory thus formulated is applied to the case of the dissociation of ammonia and ammonium chloride, when both are present in the same solution, in order to interpret the influence which ammonium salts have in retarding the saponification of ethyl acetate by ammonia, and which is in connection with the reduction of the conductivity of ammonia by ammonium salts. The theory is also extended so as to apply to the case of any number of electrolytes in solution, and leads to results similar to those which have been obtained from reasoning based on thermodynamical principles. The author concludes that the properties of dilute solutions generally, may be deduced from Van't Hoff's analogy between the gaseous state and the state of solution and the hypothesis of the dissociation of electrolytes. H. C.

Experiments on the Diffusion of Aqueous Solutions. By J. D. R. SCHEFFER (*Zeit. physikal. Chem.*, **2**, 390—404).—The solutions were allowed to diffuse in a cylindrical vessel, the diffusate being divided into four equal layers, and the amount of dissolved substance in each determined. By means of Stefan's tables, the coefficient of diffusion k of each solution was then calculated. For HCl, nOH_2 the value of the coefficient rises with the concentration from $n = 10$ to

$n = 4.5$, k being for the first, at 0° about 1.8, and for the second about 2.4. There is a rise with the concentration, for the weaker solutions also, but it is not so marked. Concentrated hydrochloric acid solutions diffuse more rapidly into solutions of weak hydrochloric acid than into water. This is explained on the hypothesis that concentrated solutions contain molecular aggregates of hydrochloric acid with relatively small quantities of water, and that on dilution, molecular aggregates richer in water are formed, this action being the more complete the greater the dilution. The results further show that the coefficient of diffusion of nitrates and some other salts, such as sodium thiosulphate and magnesium sulphate, decreases with rising concentration of the solution, whereas for nitric and sulphuric acids and calcium chloride it increases as with hydrochloric acid, although not to anything like the same extent. The author looks on this change in the value of the coefficient with changing dilution as due to molecular actions between the dissolved substance and the water. The fact that the coefficient becomes more nearly constant when a concentrated solution diffuses into a weaker solution of the same salt instead of into water, is given in support of this, since it may be assumed that in the former case the molecular aggregates have not to undergo such far reaching changes as in the latter. The coefficients also approximate to constants as the dilution of the solutions examined increases, which may be traced to the same cause. Generally, then, the coefficients of diffusion of concentrated solutions are by no means constant, and for purposes of comparison with other properties, the coefficients of dilute solutions can alone be employed.

H. C.

Vapour-tensions of Ethereal Solutions. By F. M. RAOULT (*Zeit. physikal. Chem.*, 2, 353—373).—For solutions in ether of substances whose vapour-tension is very small in comparison with that of the ether, the law holds $100 f'/f = 100 - kN$, where f is the vapour-tension of ether and f' that of the solution at the temperature of the experiment, N the number of molecules of substance in 100 mols. of the solution, and k a constant depending on the nature of the dissolved substance. The substances examined, with the values found for k , are turpentine 0.90, aniline 0.90, ethyl benzoate 0.90, methyl salicylate 0.82, and nitrobenzene 0.70. It will be seen that the values of k do not alter greatly for different substances. For dilute solutions in which N is not greater than 15, the value of k for all substances may be taken as unity. This does not hold for N less than 2, in which case the law appears to be more complicated, but this might be due to the increased difficulty of experimenting. If instead of the number of molecules of the dissolved substance, the number of molecules of ether in 100 mols. of the solution $N' = 100 - N$ be taken, and the value of k is unity, the law takes the simple form $100 f'/f = N'$, or in other words, the tension of the ether vapour of dilute ethereal solutions depends simply on the number of ether molecules in 100 mols. of the solution, and is quite independent of the nature of the dissolved substance. For concentrated solutions in which N is greater than 70, small variations

from the law which occur, may probably be due to the increase in the difficulties and errors of experiment. The law is independent of the temperature between the limits 0° and 20° .

The relation $100 f'/f = 100 - kN$ may also take the form $(f - f')/f = kN/100$. Calling $(f - f')/f$ the relative decrease in the vapour-tension, we find then that for all ethereal solutions this number is simply proportional to the number of molecules of the substance dissolved in 100 mols. of the solution. Since for $N < 15$ we get $k = 1$, and therefore $(f - f')/fN = 0.01$, we find also that the relative decrease in the vapour-tension of a dilute ethereal solution, divided by the number of molecules of non-volatile substance in 100 mols. of the solution, is equal to the constant quantity 0.01. This relation was tested with a number of substances differing widely in chemical composition, and found to hold good within experimental error. It may be used for determining the molecular weights of substances soluble in ether, for if the weight p of a substance of molecular weight M be dissolved in 100 grams of ether, then $M = 0.74 f'p/(f - f')$. The author does not, however, recommend the method, both on account of the experimental difficulties and the fact that it can only be used for substances which boil above 150° ; as a means of determining molecular weights, therefore, it cannot be compared with the cryoscopic method.

H. C.

Vapour-tension of Dilute Solutions of Volatile Substances.

By M. PLANCK (*Zeit. physikal. Chem.*, 2, 405—414).—If n and n_1 be the number of molecules of the solvent and the dissolved substance in a dilute solution, the vapour of which contains n' and n'_1 of each, then the concentration of the dissolved substance in the solution is given by $c_1 = n_1/(n + n_1)$, and in the vapour by $c'_1 = n'_1/(n' + n'_1)$, and from the conditions of equilibrium $c_1 - c'_1 = \log K$ and $\log c'_1/c_1 = \log K_1$, where K and K_1 are both functions of the temperature θ and the pressure p . The values of the functions are unknown, but the differential coefficients may be calculated, and are for both K and K_1 , of the forms $\delta(\log K)/\delta\theta = Q/\theta^2$ and $\delta(\log K)/\delta p = -V/\theta$, Q being the amount of heat, measured mechanically, which is given to the system at constant temperature θ and pressure p , in order to establish the above conditions of equilibrium, and V the attendant alteration in volume.

For the equation $c_1 - c'_1 = \log K$, the value of K may be calculated in terms either of p or of θ , by introducing the vapour-tension p_0 of the pure solvent at the temperature θ , or the boiling point θ_0 of the pure solvent at the pressure p , and expanding in powers of $(p - p_0)$ or $(\theta - \theta_0)$. The first gives $c_1 - c'_1 = (p_0 - p)/p_0$, the second $c_1 - c'_1 = (\theta - \theta_0)Q/\theta_0^2$. The first of these relations expresses in words that the relative decrease in the vapour-tension is equal to the difference in the concentration of the dissolved substance in the liquid and in the vapour. The author has calculated the values which it gives for c'_1 for the two cases of formic acid in water, where $p_0 > p$, and for isobutyl alcohol in water, where $p_0 < p$, from observations of the vapour-tension by Konowaloff. It is obvious that according as p is greater or less than p_0 , that the amount of the dissolved substance in

the liquid is less or greater than in the vapour, and that the concentration will be the same in both when $p = p_0$, a result which has already been enunciated by Konowaloff (*Ann. Phys. Chem.* [2], 14, 48). For non-volatile substances $c_1' = 0$, and we get the well-known law of the molecular reduction of the vapour-tension; for insoluble gases $c_1 = 0$ and $c_1' = (p - p_0)/p$, where $p - p_0$ is the pressure exercised by the gas, and p_0 that of the solvent in the mixed vapour, the equation shows that the pressures are proportional to the concentrations, since that of the solvent is very nearly unity, which is Dalton's law. The second relation $c' - c_1' = (\theta - \theta_0)Q/\theta_0^2$ expresses, if Q be taken for simplicity as the heat of vaporisation of 1 mol. of the solvent, that the difference in the concentration of the dissolved substance in the liquid and in the vapour is equal to this quantity multiplied by the rise and divided by the square of the boiling point. The values of c_1' have been calculated from this relation, also for aqueous solutions of formic acid and isobutyl alcohol, and are found to agree very well with those calculated by the first.

From the equation $\log c_1'/c_1 = \log K_1$ the value of c_1' may be obtained by substituting the known value of $d \log K_1$ for $d\theta$ and dp , but the expression contains Q and V , the relations of which to one another are unknown, and it cannot therefore be used practically.

All the above relations are only applicable on the assumption that the molecules of the dissolved substance are in their normal condition, and are neither dissociated nor combined one with another. They also only apply in the case of dilute solutions, but within these limits they include the most extreme cases, both those in which the dissolved substance is non-volatile and those in which it is absolutely volatile as for insoluble gases.

H. C.

A Criticism on "The Arrangement in Space of the Atoms in the Molecules of Organic Compounds." By A. MICHAEL (*J. pr. Chem.* [2], 38, 6—39).—The author argues that the agreement between experiment and theory in the phenomena studied by Wislicenus and explained by his extension of Van't Hoff's hypothesis (*Abhandlung. der K. Sächs. Gesell. der Wiss.*, 1887) is only apparent, and is based partly on unjustifiable assumptions, partly on one-sided explanations, and partly on the omission of a large number of facts which would lead to exactly contrary conclusions; and shows that for many substances as many as three different configurations are equally probable.

F. S. K.

The Different Forms of Heterogeneous Chemical Equilibrium. By H. W. B. ROOZEBOOM (*Rec. Trav. Chim.*, 6, 262—303; compare Roozeboom, *Rec. Trav. Chim.*, 5, 408).—The term "transition point" should be reserved for single points in heterogeneous equilibria, which present the greatest analogy with triple points in physical equilibria; such points are not confined exclusively to the equilibrium of condensed systems. As the transition point varies with the pressure, in order to render Van't Hoff's definition (*Zeit. physikal. Chem.*, 1, 166) correct it would be necessary to add "at constant pressure," or "at the pressure of one atmosphere." In the latter case, transition points.

which only exist under a higher pressure (compare Roozeboom, *Rec. Trav. Chim.*, **5**, 396) would be excluded, and in the former case the definition would include the whole series of temperatures at which equilibrium between liquid and solid systems is possible, but would at the same time lose all that is characteristic of the transition point.

The distinctive feature in the equilibrium of condensed systems is the absence of gaseous compounds, but such equilibria belong, nevertheless, to the category of heterogeneous equilibrium. The equilibrium of condensed systems presents a special form which is best compared to the physical equilibrium between the solid and the liquid state of the same substance, and amongst the examples of heterogeneous equilibrium those which are analogous to the volatilisation of solids can be distinguished from those which are more comparable to the evaporation of liquids.

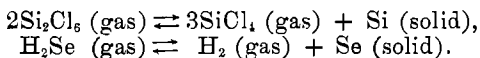
Equilibria differ also in the degree of heterogeneousness. In equilibria of systems formed of a single substance, no distinction is necessary, but in those formed of two or more substances, the degree of heterogeneousness is judged best by a comparison of the number of constituent substances which enter into the system with the number of coexistent phases, that is to say, with the different heterogeneous complexes into which one or more of the substances of the system enter, either in definite combination or in variable proportions. These phases may differ in state (solid, liquid, gaseous) and in composition, as far as it concerns liquid and solid states in which two or more complexes may coexist unmixed.

Gibbs has shown (*Trans. Connect. Acad.*, **3**, 152) that a perfectly definite state of equilibrium exists when there are $n + 1$ phases of n substances. The coexistence of $n + 1$ phases is, therefore, the necessary and sufficient condition for having at a constant temperature a state of equilibrium in which the pressure and the composition of the liquid and gaseous phases remain constant independently of the volume. The author names this state complete heterogeneous equilibrium. There is incomplete heterogeneous equilibrium when there are n substances in less than $n + 1$ phases. Complete becomes, therefore, incomplete heterogeneous equilibrium when one or more of the phases are suppressed or disappear owing to a change of temperature or pressure; as the number of phases decreases, heterogeneous equilibrium becomes more and more incomplete, until homogeneous equilibrium is established.

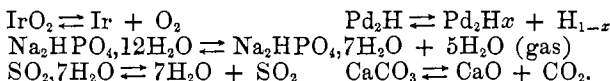
The author classifies the phenomena of dissociation according to the physical state of the coexistent phases, into three divisions (I, II, III), which are comparable to one of the three forms of physical heterogeneous equilibrium, and can be expressed by the symbols solid \rightleftharpoons vapour, liquid \rightleftharpoons vapour, solid \rightleftharpoons liquid. Each class is then subdivided (1, 2, 3, &c.) according to the number of substances which enter into equilibrium, and again subdivided (A, B, C, &c.) according to the degree of heterogeneousness as indicated by the number of coexistent phases.

I. *Volatilisation and Analogous Chemical Equilibria.*—(1.) Systems formed of a single substance. Examples:—The isomeric and polymeric transformations of substances which can exist in the gaseous

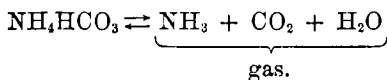
state, for instance, paracyanogen, amorphous phosphorus. (2.) Systems formed of two substances. (A.) Incomplete equilibrium between one solid and one gaseous phase. Examples:—The absorption of gas by solids (charcoal and certain metals), or the absorption of hydrogen by metallic hydrides (Pd_2H , K_2H). The decomposition of ammonium carbamate, phosphorus pentachloride, mercuric oxide, &c. The phenomena studied by Troost and Hautefeuille (*Ann. Chim. Phys.* [5], 7, 452), and by Ditte (*Ann. Scient. École Norm.* [2], 1, 293), of the volatilisation of a simple substance into a gas, with which it can enter into chemical combination, for instance:—



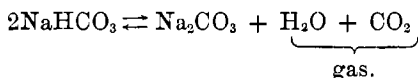
(B.) Complete equilibrium between two solid and one gaseous phase. Examples:—The decomposition of solids into one solid and one gaseous constituent—



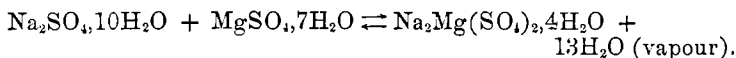
(3.) Systems formed of more than two substances. (A.) Incomplete equilibrium between one gaseous and one solid phase. Example:—



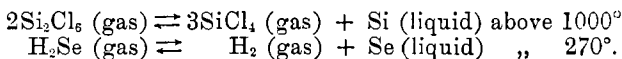
(B.) Incomplete equilibrium between one gaseous and two solid phases. Example:—



(C.) Complete equilibrium between one gaseous and three solid phases. Example:—



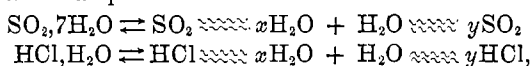
II. *Evaporation and Analogous Chemical Equilibria.*—(1.) Systems formed of a single substance. Example:—A liquid and its vapour. (2.) Systems formed of two substances. (A.) Incomplete equilibrium between one gaseous and one liquid phase. Examples:—The solution of a non-volatile substance in a liquid. A liquid and its vapour, the gas enclosing the two constituents at least partially uncombined. The decomposition of a gas into one liquid and one gaseous substance, for instance—



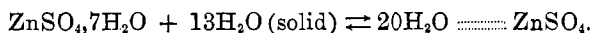
(B.) Complete equilibrium between two liquid and one gaseous phase. Examples:—Physical equilibrium between two only partially miscible liquids and their vapours. (C.) Complete equilibrium between one liquid, one solid, and one gaseous phase. Examples:—Equilibria into

which the hydrates of a gas, the compounds of ammonium salts with ammonia, and the compounds of selenious acid with hydrochloric and with hydrobromic acid enter in the solid state (compare *Rec. Trav. Chim.*, **4**, 361, and **5**, 387). Equilibrium between a salt, its solution, and the vapour of the solvent. (3.) Systems formed of more than two substances. (A.) Complete equilibrium between three liquids and their vapours. Examples unknown. (B.) Complete equilibrium between one gaseous, two liquid, and one solid phase. Examples:—The equilibria studied by Forcrand (*Ann. Chim. Phys.* [5], **28**, 9), in which the solid is a compound consisting of water, hydrogen sulphide, and some chloro-, bromo-, or iodo-derivative of an organic fatty compound, and constituted after the type $\text{CHCl}_3, 2\text{H}_2\text{S}, 23\text{H}_2\text{O}$. (C.) Complete equilibrium between two solid, one liquid, and one gaseous phase. Example:—Two salts in their saturated aqueous solutions. (D.) Incomplete equilibrium between two liquid and one gaseous phase. Examples unknown. (E.) Incomplete equilibrium between one solid, one liquid, and one gaseous phase. Example:—A solution of two salts, of which one only is in excess. Solutions of alkaline bicarbonates, double salts, acid salts, and basic salts, which are decomposed by water. (F.) Incomplete equilibrium between one liquid phase and one gaseous phase comprising three substances. Examples unknown.

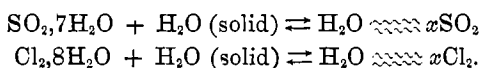
III. *Fusion and Analogous Chemical Equilibria*.—(1). Systems formed of a single substance. Example:—Equilibrium between the two modifications of one substance. (2.) Systems formed of two substances. (A.) Complete equilibrium between one solid and two liquid phases. Examples:—



(the sign sol signifies the state of solution). (B.) Complete equilibrium between one liquid and two solid phases. Examples:—Ice and a salt, which exist together in presence of a solution of a salt at the cryohydric point under the pressure of one atmosphere, but which can also exist at a lower temperature if the pressure is increased, for instance—



Also equilibria such as—



(C.) Complete equilibrium between three solid phases. Examples unknown. (D.) Incomplete equilibrium between one solid phase and one liquid phase comprising two constituent substances. Examples:—A solution of $\text{Br}_2\text{H}_2\text{O}$ (compare Roozeboom, *Rec. Trav. Chim.*, **5**, 362). (E.) Incomplete equilibrium between two liquid phases. Examples unknown.

(3.) Systems formed of more than two substances. (A.) Complete equilibrium between three solid and one liquid phase. Examples:—A double salt, its two constituents, and an aqueous solution. Examples

of complete equilibrium between (B) two solid and two liquid phases, (C) one solid and three liquid phases, and (D) four solid phases, are unknown. F. S. K.

Triple and Multiple Points regarded as Transition Points.

By H. W. B. ROOZEBOOM (*Rec. Trav. Chim.*, 6, 304—332; compare preceding Abstract).—The transition point is the point of intersection of two curves of equilibrium for $n + 1$ phases of which n are equal, so that $n + 2$ phases can exist in this point. But these same $n + 2$ phases can be arranged in $n + 1$ systems of $n + 1$ phases, so that this same point must be a final point of $n + 1$ curves. For each of these equilibria, a single phase disappears when the system arrives at the point of transition.

The author discusses, with the aid of diagrams, the signification of the triple point in physical equilibria, and in cases of chemical equilibria, such as the conversion of rhombic into monosymmetric sulphur, classified according to the number of coexistent phases, and concludes as follows:—A triple point represents the only temperature and pressure which render possible the coexistence of three heterogeneous phases of the same substance. Three curves meet at this point representing the equilibria of the three systems of two phases which can be formed from these three phases. These curves divide the diagram (*p.t.*) into three regions, one for each phase. When heat is supplied to or taken from the system, we pass from the triple point on to one of the three curves by the disappearance of one of the phases owing to a transformation in which all three participate. In one direction, this phase is determinate, but in the other it may be one of the remaining two according to their proportionate quantities. The triple point is always a transition point in one direction for a single phase. Where one of the three phases at the triple point is a gas, this point may also be a transition point in the other direction, provided that the gaseous phase is in excess. The triple point is a limit of temperature for those phases which disappear entirely. There is one curve on one side of the triple point, and two on the other. The triple point is a transition point in the direction in which there is only one curve, and the phase which disappears is the one the region of which is comprised between the remaining two. The triple point is a limit for each of the three curves.

Quadruple Points.—Compare Roozeboom (*Rec. Trav. Chim.*, 5, 393). If A, B, C are the three phases of two substances, and if the change which takes place at constant pressure when heat is supplied to or taken from the system, be expressed thus, $A \rightleftharpoons B + C$, from one point of the curve, it is only possible to pass to a higher temperature after the total disappearance of A. On the other hand, when heat is taken from the system, B + C are changed into A, but it will depend on their relative quantities which of the two phases will subsist with A to the left of the curve, A + B or A + C. A consideration of the transformation produced by change of pressure at constant temperature leads to the same conclusions, so that whereas there is only one region for a single phase on the two sides of a curve for two phases, the region of two of the three phases lies on one side

of a curve for three phases; the region for the two other systems of two phases lies on the other side. The author discusses, with the aid of diagrams, the signification of the quadruple point in equilibria classified according to the number of coexistent phases (compare Roozeboom, *Rec. Trav. Chim.*, 5, 396), and concludes as follows:—The quadruple point is the only point (*p.t.*) in which four heterogeneous phases, into the composition of which two substances enter, can coexist in equilibrium. Four curves, each for three phases, meet in these points and divide the diagram (*p.t.*) into six regions for the six groups of two phases which can be formed. If heat is taken from or supplied to the system of four phases in the quadruple point, there is a transformation in which all four phases participate, and which terminates in the disappearance of one of them in each direction. The composition and specific volume of the phases must be known before the equation of this transformation can be given, as it takes place at constant volume. There are two cases possible: the equation may contain two phases on each side, or one phase on one side and three on the other. In the first case, there are two phases which can disappear in each direction, in the second case one phase only disappears in one direction and one of three phases in the other. When two or three phases can disappear, it depends on their proportionate quantities which does so. The quadruple point can be a transition point for, at the most, one phase in one direction, but it is not so always; and in the case of a liquid phase the quadruple point is a transition point only when the triple point is a transition point for a liquid between two limits of concentration. If one of the phases is gaseous, the quadruple point can always be a transition point for one of the other phases, provided that the gaseous phase is present in sufficient quantity. By the disappearance of one of the phases, when heat is taken from or supplied to the system, we pass from the quadruple point on to one of the four curves for three phases. Of these curves, there may be two on each side of the quadruple point, or one on one side and three on the other. In the first case, the quadruple point is an inferior limit of temperature for one system of two phases, and a superior limit for the other system of two phases. In the second case, the quadruple point is a limit for three regions of two phases situated on the same side and comprised between the three curves, whereas in the inverse direction it is a transition point for the phase which is common to these three regions. Each of the four curves of three phases which meets at the quadruple point has a limit.

Quintuple Points.—In a system of five phases formed of three constituent substances there is complete heterogeneous equilibrium when there are four coexistent phases. This equilibrium will be expressed by a curve (*p.t.*). The transformation which would take place at a point of such a curve, either by a variation of pressure at constant temperature or by a variation of temperature at constant pressure, would be completed by the disappearance of one of the four phases.

If A, B, C, D are the four phases, the transformation may take place thus: $A + B \rightleftharpoons C + D$; or thus: $A \rightleftharpoons B + C + D$. In the first case the phases $A + B + C$ and $A + B + D$ could exist on one side of

the curve, and the phases $A + C + D$ and $B + C + D$ on the other. In the second case $A + B + C$, $A + B + D$, and $A + C + D$ on one side and $B + C + D$ on the other. The curve can therefore divide the diagram into two regions for two systems of three phases, or into one region for one system and another in which three systems of three phases can exist. If two of these curves meet, there results a quintuple point in which three other curves terminate, together dividing the diagram into six regions for the ten groups of three phases which can be formed from the five phases coexisting in the quintuple point. The five curves can be situated to the right or to the left of the quintuple point 1 to 4 or 2 to 3, but the quintuple point is a transition point for a single phase only in the first case. F. S. K.

Osmotic Experiments with Living Membranes. By H. DE VRIES (*Zeit. physikal. Chem.*, 2, 415—432).—This paper contains a description of the method used for determining the isotonic coefficients of solutions by observation of their behaviour towards plant-cells. The cells used are those of the leaves of *Tradescantia discolor*, *Curcuma rubricaulis*, and *Begonia manicata*. Viewed under the microscope, these cells are seen to consist of an outer sheath, which is rigid and defines the shape of the cell, being either tetragonal or hexagonal, containing the sap of the cell inclosed within an inner membrane. The outer sheath is permeable for water or aqueous solutions, the inner membrane for water alone and not for dissolved substances, fulfilling the conditions of a semi-permeable material. The inner membrane being elastic will follow by contraction or expansion any change in the volume of the sap which it incloses. In the normal condition, the sap, which is highly coloured for the above plants, fills the whole of the cell, the inner membrane being pressed closely against and indistinguishable from the inner side of the outer sheath. If the cell is immersed in an aqueous solution, this will permeate the outer sheath, and if its osmotic pressure is greater than that of the sap, water will pass through the walls of the inner membrane from the latter to the solution. The volume of the sap therefore decreases and a contraction will take place, the inner membrane leaving the sides of the outer sheath and being drawn together round the coloured sap, the spaces thus rendered vacant becoming filled with the colourless solution, a change easily observed under the microscope. By reducing the strength of the solution, the osmotic pressure decreases and the contraction may be brought down to a minimum; and finally when the osmotic pressure of the solution and the sap are the same, the contraction ceases to occur, and no change in the appearance of the cell takes place on immersion. A solution of this strength is then said to be isotonic with the sap, and of course those solutions isotonic with the sap of the same cells are isotonic with one another. The comparison of relations of the concentrations of isotonic solutions to one another gives their isotonic coefficients, that of potassium nitrate having been taken for physiological reasons as the standard and assumed equal to 3.

It must be pointed out that a cell immersed in a solution, the strength of which is below that of the isotonic, will undergo no

change in appearance, for, although water is absorbed by the sap, the rigidity of the cell walls prevents expansion taking place. In practice, it is customary to reduce the difference between the strengths of solutions which are observed to be above that of the isotonic and of those which are known to be beneath it to a minimum, and then to take the mean. The inner membranes were found to be practically impermeable for all the neutral substances examined, except that of the *Tradescantia* for glycerol, the exception here being due to some unknown physiological action. Acids, alkalis, and other substances which in any way chemically attack the cell cannot of course be examined.

A table is given of the isotonic coefficients of a number of substances; and a comparison of the same made with the molecular reduction of the freezing point and the vapour-tension, from which it appears that solutions of equal osmotic pressure have the same freezing point and the same vapour-tension. Osmotic pressure being, according to Van't Hoff, proportional to the molecular weight, a calculation of the extent to which dissociation of certain electrolytes in solution takes place is made, the results of which agree on the whole with those of Arrhenius. A determination of the molecular weight of raffinose gave for this the formula $C_{18}H_{32}O_{16}, 5H_2O$. H. C.

The Laws Governing the Reactions of Direct Addition. By I. KABLUKOFF (*J. Russ. Chem. Soc.*, 1887, 566—585).—When halogen hydrides unite with unsaturated hydrocarbons, the combination takes place according to a law which was first enunciated by Markownikoff as follows:—In the case of the combination of unsymmetrical hydrocarbons with halogen acids, the halogen combines with the carbon-atom in union with the smallest number of hydrogen-atoms, that is, with the carbon-atom which is most influenced by other carbon-atoms. The same rule holds good when the addition of sulphuric acid takes place. The author shows in several tables that the reactions depend on the heat of formation of the resulting compounds; the heat of formation of the tertiary alcohols and the corresponding compounds, for instance, is larger than that of their secondary and primary isomerides. When the halogen unites with the least hydrogenised carbon-atom, more heat is evolved than would be the case if it were added to the other side of the double linking. The reaction taking place is in accordance with Berthelot's principle of maximum of work.

According to Potilizin's investigations, however, the reaction which takes place at a higher temperature is the reverse of that which is found to take place at low temperatures. This is explained by a second empirical law of Markownikoff, namely: When an unsaturated molecule, C_mH_nX , combines with a saturated one, YZ , at a low temperature, the negative element or group will combine with the least hydrogenised carbon-atom, or with a carbon-atom already in union with a negative element or group, whereas at a higher temperature the reverse order of combination takes place. The addition of hypochlorous acid forms an exception, as it only in some cases follows this rule; sometimes the distribution of its elements takes place in both directions.

When organic oxides combine with the halogen hydrides, the halogen

combines with the least hydrogenised carbon-atom, and the hydroxyl-group is formed at the most hydrogenised carbon-atom. All these changes take place in accordance with the thermochemical data.

B. B.

Method for avoiding "Bumping" in Distillation. By W. MARKOWNIKOFF (*J. Russ. Chem. Soc.*, 1887, 520—521). The disagreeable phenomenon of "bumping" is avoided only for some little time after boiling commences when platinum wire or pieces of charcoal, &c., are introduced into the liquid. The author finds that good results are obtained on coating the inside of the vessel with a thin layer of silver; this, however, easily breaks off. A far better method is to introduce into the liquid a few very thin capillary glass tubes of 3 to 10 mm. in length, and sealed up at one end. The boiling then goes on quietly at ordinary or reduced pressure, even if a finely divided precipitate like barium sulphate occurs in an aqueous solution of a salt. Even such liquids as caustic soda may be boiled easily when these tubes are used.

Note.—The Abstractor has tried the device above suggested and found it invaluable, especially for the distillation of concentrated acids. He recommends that the capillary tubes be made of different sizes so that they may float in different layers of the liquid.

B. B.

New Apparatus. By C. LIEBERMANN (*Ber.*, 21, 2528—2529).—
1. *Apparatus for Fusion with Potash.*—The fusion is conducted in a nickel dish supported on a copper-bath constructed on the principle of V. Meyer's drying apparatus. The bath contains naphthalene, anthracene, or anthraquinone, &c., and is provided with a condenser.

2. *Desiccator for Substances Sensitive to Light.*—The desiccators are made of thick, brownish-yellow glass of the sort used for photographic dark rooms. Funnels, plates, and crystallising dishes of the same glass are also useful.

3. *Arrangement for Water-pumps.*—Nickel-plated water-pumps are screwed to one end of the bench; the outlet is soldered into a waste-pipe.

N. H. M.

Inorganic Chemistry.

Sulphur Compounds. By H. REBS (*Annalen*, **246**, 356—382).
—Hydrogen persulphide, prepared by pouring aqueous solutions of potassium, sodium, or barium polysulphides into an excess of hydrochloric acid, always have the composition H_2S_5 . The sp. gr. of the compound is 1.71 at 15° .

The author has obtained the compounds P_2S_5 and P_4S_3 in the crystalline form by heating a mixture of phosphorus and sulphur in the theoretical proportions and extracting the product with carbon bisulphide. The trisulphide, P_2S_3 , is sparingly soluble in carbon bisulphide.

A comparison of the barium-derivatives of methyl and ethyl hydrogen sulphates prepared by (1) the action of water on methyl or ethyl sulphate, and (2) by the action of sulphuric acid on ethyl or methyl alcohol shows that the salts obtained from the different sources are identical. Church's statement (*Chem. Centr.*, 1856, 146) that the salts are isomerides is incorrect.

The author agrees with Weber (*Ann. Phys. Chem.*, **159**, 313) that Marignac's (*Ann. Phys. Chem.*, **139**, 480; *Jahresb.*, 1879, 209) isomeric modification of sulphuric anhydride is in reality a compound of the anhydride with a small quantity of water. W. C. W.

Dithionates. By K. Klüss (*Annalen*, **246**, 179—220 and 284—306).—When freshly precipitated bismuth hydroxide is treated with dithionic acid, an acid solution is formed which, on evaporation, deposits monoclinic crystals of the basic salt, $\text{Bi}_2\text{S}_2\text{O}_8 + 5\text{H}_2\text{O}$. If the acid solution is poured into water at 60° , a more basic salt, $4\text{Bi}_2\text{O}_3 \cdot 3\text{S}_2\text{O}_5 + 5\text{H}_2\text{O}$, is precipitated.

Normal stannous dithionate can exist in solution, but has not been isolated. If the solution is poured into water, a basic salt, $8\text{SnO}_2 \cdot \text{S}_2\text{O}_5 + 9\text{H}_2\text{O}$, is deposited. The normal thorium dithionate, $\text{Th}(\text{S}_2\text{O}_6)_2 + 4\text{H}_2\text{O}$, is very unstable, and decomposes at the ordinary temperature with evolution of sulphur dioxide. Normal chromic dithionate, $\text{Cr}_2(\text{S}_2\text{O}_6)_3 + 18\text{H}_2\text{O}$, is obtained in octohedra when freshly precipitated chromic hydroxide is digested with a slight excess of dithionic acid. If the oxide is in excess, a green, amorphous basic salt, $3\text{Cr}_2\text{O}_3 \cdot 4\text{S}_2\text{O}_5 + 24\text{H}_2\text{O}$, is produced. Uranium yields three basic dithionates of the composition $7\text{UO}_2 \cdot \text{S}_2\text{O}_5 + 8\text{H}_2\text{O}$; $6\text{UO}_2 \cdot \text{S}_2\text{O}_5 + 10\text{H}_2\text{O}$, and $8\text{UO}_2 \cdot \text{S}_2\text{O}_5 + 21\text{H}_2\text{O}$. Ammonium dithionate, $(\text{NH}_4)_2\text{S}_2\text{O}_6 + \frac{1}{2}\text{H}_2\text{O}$, crystallises in needles belonging to the monoclinic system. A basic beryllium salt, $5\text{BeO} \cdot 2\text{S}_2\text{O}_5 + 14\text{H}_2\text{O}$, is obtained as a gummy mass on carefully evaporating a solution of beryllia in dithionic acid.

Ferrous dithionate, $\text{FeS}_2\text{O}_6 + 7\text{H}_2\text{O}$, forms triclinic prisms. At 18.5° 1 part of salt dissolves in 0.59 of water. The normal ferric dithionate has not been isolated; a solution of the salt decomposes, yielding ferric sulphate, ferrous dithionate, sulphurous oxide, and sulphuric acid. If the solution is poured into water at 70° , a basic salt, $8\text{Fe}_2\text{O}_3 \cdot \text{S}_2\text{O}_5 + 14\text{H}_2\text{O}$, is deposited in the form of a brownish-red powder. Hydrogen peroxide converts ferrous dithionate into two basic salts, $3\text{Fe}_2\text{O}_3 \cdot \text{S}_2\text{O}_5 + 8\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 2\text{S}_2\text{O}_5$. The normal cobalt salt, $\text{CoS}_2\text{O}_6 + 8\text{H}_2\text{O}$, forms triclinic crystals. It is deposited from alcoholic solution in pink prisms containing only 6 mols. H_2O . Normal copper dithionate crystallises with 4 and also with 5 mols. H_2O . A basic salt, $4\text{CuO} \cdot \text{S}_2\text{O}_5 + 4\text{H}_2\text{O}$, insoluble in water, is formed when the normal salt is digested with freshly precipitated cupric hydroxide. Another basic salt, $4\text{CuO} \cdot \text{S}_2\text{O}_5 + 3\text{H}_2\text{O}$, is prepared by slowly raising the temperature of a dilute solution of copper acetate and sodium dithionate to 70° .

Mercuric dithionate, $\text{HgS}_2\text{O}_6 + 4\text{H}_2\text{O}$, is an unstable, crystalline compound. It is occasionally formed by digesting precipitated mercuric oxide in dithionic acid, but the exact conditions under which it is produced are not known. Aluminium dithionate, $\text{Al}_2(\text{S}_2\text{O}_6)_3 +$

$18\text{H}_2\text{O}$, forms transparent, deliquescent plates soluble in water and in alcohol. Dithionic acid does not act on ceric and thallic hydroxides at the ordinary temperature; at a higher temperature, the acid decomposes. A solution containing sodium and thallium in molecular proportion deposits rhombic crystals in which the proportion of Tl_2O to Na_2O is as 9 : 4. A mixture of lithium and thallium dithionates deposits monoclinic prisms, $\text{Tl}_2\text{O} : \text{Li}_2\text{O} = 3 : 4$.

The following mixed salts were also obtained: $2\text{Tl}_2\text{S}_2\text{O}_6 \cdot \text{Ag}_2\text{S}_2\text{O}_6$, apparently triclinic; $3\text{Tl}_2\text{S}_2\text{O}_6 \cdot 2\text{BaS}_2\text{O}_6$; $2\text{ZnS}_2\text{O}_6 \cdot 9(\text{NH}_4)_2\text{S}_2\text{O}_6 + 16\frac{1}{2}\text{H}_2\text{O}$, monoclinic; $\text{ZnS}_2\text{O}_6 \cdot 5(\text{NH}_4)_2\text{S}_2\text{O}_6 + 9\text{H}_2\text{O}$; $\text{CdS}_2\text{O}_6 \cdot 2(\text{NH}_4)_2\text{S}_2\text{O}_6 + 4\frac{1}{2}\text{H}_2\text{O}$, monoclinic; $\text{FeS}_2\text{O}_6 \cdot 3(\text{NH}_4)_2\text{S}_2\text{O}_6 + 6\text{H}_2\text{O}$, monoclinic; and $2\text{FeS}_2\text{O}_6 \cdot 9(\text{NH}_4)_2\text{S}_2\text{O}_6 + 16\frac{1}{2}\text{H}_2\text{O}$; manganese ammonium dithionate, $2\text{MnS}_2\text{O}_6 \cdot 9(\text{NH}_4)_2\text{S}_2\text{O}_6 + 16\frac{1}{2}\text{H}_2\text{O}$, and the nickel and cobaltammonium salts are isomorphous with the zincammonium salt. The copper salt is not isomorphous, although it crystallises in the monoclinic system. Its formula is $2\text{Cu}_2\text{S}_2\text{O}_6 \cdot (\text{NH}_4)_2\text{S}_2\text{O}_6 + 8\text{H}_2\text{O}$. $\text{Al}_2(\text{S}_2\text{O}_6)_3 + (\text{NH}_4)_2\text{S}_2\text{O}_6 + 27\text{H}_2\text{O}$ forms deliquescent, monoclinic crystals. W. C. W.

Colloïds and the Water they Contain. By J. M. VAN BEMMELEN (*Rec. Trav. Chim.*, 7, 37—68).—A colloïd that feels dry still contains a considerable quantity of water, and when further dried at a constant temperature, the state of aggregation is continuously modified and with it the composition. When, at a certain temperature, a colloïd has lost so much water that its vapour-tension is equal to that of water at the same temperature, any further loss of moisture can be prevented by placing it in a closed space in proximity to water and keeping the temperature constant. If a colloïd, after exposure to dry air, has lost so much water that its vapour-tension has become practically null, it can regain its water either partially or entirely when placed in an atmosphere saturated with aqueous vapour, but the whole of the water can be regained only when the change in the state of aggregation is completely reversible. In a closed space partially saturated with moisture, a colloïd loses water until its vapour-tension is equal to that in the surrounding medium. The rapidity of dehydration in a dry medium at a constant temperature continually diminishes until it reaches a minimum, for instance, colloïdal metastannic acid containing 2.2 mols. H_2O , lost 0.55 mol. H_2O the first day, and this quantity gradually decreased to 0.01 mol. H_2O on the thirteenth day, when the composition was 0.79 mol. H_2O .

A colloïd loses or attracts moisture with decreasing rapidity until its vapour-tension is equal to that of water, and as a rule no definite hydrate is formed when it loses water. At every temperature, a colloïd attains a different final composition either in dry air or in an atmosphere saturated with moisture. The non-reversible modifications which most colloïds undergo in losing water, or when heated, complicate the process of dehydration or rehydration; generally the non-reversible modifications have a diminished absorptive power, but they retain their water with more energy. The vapour-tension is in this case more or less diminished.

When the temperature is raised, the decomposition of a colloïd is gradual; at first the vapour-tension increases and also the rate of

decomposition, it then decreases and reaches a minimum. The quantity of water in a colloid either in a dry or a saturated atmosphere is less than what is present at a lower temperature, and the difference is greater the more the colloid has undergone modification by the action of heat. A definite composition can be attained when a colloid is heated sufficiently long at any temperature, but the more quickly, the higher the temperature, provided the initial composition is the same in both cases; for example, with colloidal stannic acid containing about 3 mols. H_2O , the same composition (1 mol.) is attained in one hour at 103° or in several days at 15° . When the same quantity is heated successively at increasing temperatures, so long that at each temperature the decomposition attains a minimum, the rate of loss is found to vary. In the case of colloidal alumina, the rapidity increases at about 220° , in the case of colloidal glucina at 215° . These accelerations indicate a more intrinsic modification in the state of aggregation and are often accompanied by a change in colour.

Under favourable circumstances, colloids can be transformed into definite hydrates. Crystalline glucinum hydrate (compare Bemmelen, *J. pr. Chem.* [2], **26**, 227) is only slightly hygroscopic; it has a definite composition which it retains even when heated at about 200° , at 204 — 215° slight decomposition occurs which becomes relatively rapid at 215 — 220° .

The compounds described by Ditte as hydrates of vanadic acid are colloids.

For the transformation of a colloid into a hydrate or chemical compound, it must undergo modification at a suitable temperature, such that it becomes insoluble in the medium in which it was dissolved when in the colloidal state.

F. S. K.

Colloidal Silica. By J. M. VAN BEMMELEN (*Rec. Trav. Chim.*, **7**, 69—74).—Four samples of colloidal silica prepared as follows:—*a*, by acidifying a solution of an alkaline silicate; *b*, by decomposing methyl orthosilicate with water; *c*, by decomposing silicon tetrachloride; and *d*, by decomposing silicon tetrafluoride with water, were quickly dried with blotting paper, and then heated until the weight was constant, at 15° , at 100° , and at a red heat (1), in ordinary air; (2), in dry air; and (3), in air saturated with moisture. The results obtained show that the four preparations retain different quantities of water at any given temperature, and that at every temperature equilibrium is established between the vapour-tension of the colloid and that in the surrounding medium. *a* retains more water at 50° or even at 100° in a medium saturated with aqueous vapour than at 15° in dry air. *a* and *b* have the same vapour-tension as water at the ordinary temperature when they have absorbed about 4 mols. H_2O ; *c* and *d* when they have absorbed 1.8 and 2.2 mols. respectively. This tension diminishes as the water is driven off, and approaches zero when the quantity of water present is $a = 0.26$, $b = 0.36$, $c = 0.3$, and $d = 0.3$ mols. *a* absorbs and loses water most readily, and is least modified by heat, inasmuch as its absorptive power is not diminished at all after it has been heated at 100° , and in a less degree than the other preparations after moderate calcining. *b* is more stable in the

dissolved state and retains its water with more energy than *a*, *c*, or *d* in dry air at 100°, but its absorptive power is greatly diminished after having been heated at 100°. *d* is most voluminous in the dry state, and retains the least quantity of water when exposed to the air at the ordinary temperature. *a*, *b*, and *c* entirely lose their absorptive power after having been calcined at a high temperature, but *d* still absorbs a small quantity of water at 15° in an atmosphere saturated with moisture.

The author concludes that the quantity of water retained by the colloid between 15° and 100° in a damp atmosphere depends on the temperature, on the state of aggregation, and on the vapour-tension of the surrounding medium.

F. S. K.

Colloidal Alumina and Aluminium Hydrate. By J. M. VAN BEMMELEN (*Rec. Trav. Chim.*, 7, 75—87; compare Ramsay, this Jour., 1877, ii, 396, and Carnelley and Walker, *Trans.*, 1888, 54).—Four samples of colloidal alumina were prepared as follows:—*a''* by precipitating a solution of aluminium chloride with ammonia, washing for a long time and drying in the air; *a'* by precipitating a very dilute solution of aluminium chloride (1 gram Al_2O_3 in 1 litre) with ammonia, washing as quickly as possible, and exposing to the air until dry to the hand; *b* by boiling *a''* for 24 hours with a large quantity of water and then drying in the air; and *c* by keeping *a''* for six months under water and then drying in the air.

After exposure to the air at the ordinary temperature, they have all practically the same composition, namely 4.3 to 4.5 mols. H_2O , but when placed at 15° in a dry atmosphere, or in an atmosphere saturated with moisture, or when heated at 100° in the air, in all cases until equilibrium is established, the quantity of water remaining is different in each sample in every case.

When *a''* is heated at 100° in dry air, the quantity of water given off decreases from about 0.5 mol. to 0.02 mol. per hour, but the weight does not become constant even in nine hours. When the four samples are heated for 1 to 2 hours at temperatures increasing from 140° to 300°, the loss of water is different in each case, but it seems that this difference practically disappears between 250° and 300°, at which temperature they have all the approximate composition $\text{Al}_2\text{O}_3 + \text{H}_2\text{O}$. At any temperature between 15° and 300°, there is no increase or decrease in the rate of loss which would indicate the formation of a definite hydrate.

a' retains and absorbs water with more force than *a''* or *b*. Colloidal alumina becomes more sparingly soluble in acids and alkalis in proportion to the quantity of water which it loses when heated; and after heating *a* and *a''* at various temperatures, they absorb smaller quantities of water when placed in a saturated atmosphere, and they retain less in dry air in proportion to the loss of water which has occurred.

100 mols. of the dry colloid, $\text{Al}_2\text{O}_3 + 5.5\text{H}_2\text{O}$, absorb 2.5 mols. of potassium sulphate when agitated at 50° with a solution containing 30 mols. of potassium sulphate in 100 c.c.; with the same weight of colloid, the quantity of salt absorbed at a constant temperature in-

creases with the concentration and volume of the saline solution, but in a decreasing proportion.

The substance which separates from an alkaline solution of the colloid, either spontaneously or by the slow action of carbonic anhydride, is a true hydrate and a definite chemical compound, $\text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$. It is crystalline under the microscope and is only slightly hygroscopic. It remains practically unchanged when heated at 160° in a stream of dry air; between 170° and 200° it is slowly decomposed but with decreasing rapidity, so that even after 30 hours it has not attained the composition $\text{Al}_2\text{O}_3 + 2\text{H}_2\text{O}$. Between 200° and 225° , the rate of decomposition increases and 1 mol. H_2O is driven off in a few hours, but the rate of loss gradually diminishes and the final composition attained is approximately $2\text{Al}_2\text{O}_3 + \text{H}_2\text{O}$. From 225° to 320° , decomposition is excessively slow, only at a temperature above 320° does the quantity of water fall to less than half a molecule in a relatively short time.

When it is heated for an hour in a bunsen flame, and then placed in a damp atmosphere, it absorbs 3.75 mols. H_2O in 13 days, but if then kept in dry air for six days, the water falls to about 2 mols.

This hydrate does not absorb crystalline substances from their solutions.

The sample *c* referred to above is in some respects similar to a true hydrate; after exposure to the air, its composition is approximately $\text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$. When heated at 100° to 170° , it loses water very slowly until the composition becomes about $\text{Al}_2\text{O}_3 + 2\text{H}_2\text{O}$, but it is amorphous and very hygroscopic.

F. S. K.

Colloïdal Stannic Acid. By J. M. VAN BENMELEN (*Rec. Trav. Chim.*, 7, 87—106).—The same quantity of colloïdal stannic acid was agitated for 15 minutes with the same volume of cold, dilute potash of various concentrations, and from the quantity of stannic acid dissolved and the subsequent behaviour of the solutions the author concludes that no chemical combination of stannic acid with potash is formed but only complex molecules, the composition of which varies considerably with the temperature and concentration.

Four samples of colloïdal stannic acid were prepared:— a^α by dialysing a hydrochloric acid or alkaline solution of stannic acid, or by the action of calcium carbonate on an aqueous solution of the chloride; a^β by passing a stream of carbonic anhydride through an alkaline solution; a^γ by the action of an atmosphere of carbonic anhydride, and a^δ by the action of ordinary air on an alkaline solution of stannic acid.

a^α has all the properties of a colloid and appears amorphous even when magnified 750 times. A fifth sample, a^ϵ , prepared by treating an alkaline solution of stannic acid with carbonic anhydride, also appeared amorphous under the same magnifying power; it is hygroscopic and has no definite composition.

The samples a^α , a^β , a^γ and a^δ , contain different quantities of water when dry, and also after exposure to the air, or after keeping in a damp atmosphere. Colloïdal stannic acid has a vapour-tension equal to that of water at the ordinary temperature, when it contains about 3 mols. H_2O , but this quantity depends on the method of preparation,

as α^{β} , retains less than α^{β}_1 . This tension approaches zero when the water falls to about 1 mol. When α^{α} , α^{β}_1 , α^{β}_2 and α^{β}_3 are placed in dry air at about 15° , the vapour-tension and the rapidity of decomposition vary continually in all four samples, and if they are then placed in a damp atmosphere the water is only partially regained. α^{β}_2 retains more water at 55° in a damp atmosphere than at 15° in dry air; when heated at 55° in a moist atmosphere, it loses 1.12 mols. H_2O in $9\frac{1}{2}$ hours, and a further loss of 0.93 mol. takes place at 55° in dry air in 11 hours, but in both cases the rate of loss decreases with the time: α^{α} behaves similarly. At 100° , decomposition is more rapid in all the samples, but equilibrium is not established until after a long time, especially in the case of α^{β}_3 .

If the colloid has lost water by previous exposure to dry air or by heating at 55° , the decomposition at 100° takes place with greater rapidity. At 105° , 120° , and 160° , the decomposition is similar to that at 100° , the rate of loss increases with every rise of temperature and then decreases. The same ultimate composition can be attained at 15° , 55° , 100° , 105° , and 110° , but the lower the temperature the longer the time required.

Colloidal stannic acid, prepared either by saturating a freshly prepared aqueous solution of stannic chloride with carbonic anhydride, or by saturating a freshly prepared potash solution of stannic chloride with carbonic anhydride, did not give the reactions of so-called metastannic acid, even after having been dried by pressure at the ordinary temperature, but after having been heated with water below 100° , or kept some time in a stoppered flask, so that no loss of water occurs, or when heated at 55° or 100° , it no longer dissolves entirely in concentrated hydrochloric acid, and gives in a greater or less degree the reactions of metastannic acid with nitric acid, sulphuric acid, and stannous chloride.

Colloidal metastannic acid, dried at the ordinary temperature, contains 2.2 mols. H_2O , and absorbs very little water when placed in an atmosphere saturated with moisture; in dry air, the water falls to 0.8 mol., and the composition then remains practically constant. At 100° , the moisture falls to 0.68 mol. in one hour, and to 0.6 mol. after several hours.

The results obtained on heating colloidal stannic acid and metastannic acid at temperatures increasing from 15° to 185° , show that the former is gradually changed into the latter when heated. When colloidal metastannic acid, containing 2.3 mols. H_2O in an atmosphere saturated with moisture, has lost 1.5 mols. by exposure to dry air, it only regains 0.9 mol. when again placed in a saturated atmosphere; after having been heated at 100° , it only absorbs 0.7 mol.; and after having been calcined, it only regains 0.28 mol. When strongly calcined, it is no longer hygroscopic in ordinary air.

Colloidal metastannic acid does not form any definite compound with potash when treated with solutions of various concentrations. The composition of the opalescent solutions obtained varies very considerably and is greatly influenced by the concentration; the undissolved colloid absorbs some of the potash. Hydrochloric acid acts like potash, but the acid must be concentrated in order to form the

complex molecules which are again decomposed and dissolved on adding water, but are reformed and become insoluble when an excess of hydrochloric acid is added. Sulphuric acid precipitates the colloid still more readily from its solution in water or dilute hydrochloric acid (compare *J. pr. Chem.* [2], 23, 331—339). The yellow precipitate obtained with stannous chloride in a hydrochloric acid solution, and that produced by potassium ferrocyanide in a potash solution, are undoubtedly absorption compounds. F. S. K.

Colloïdal Ferric Oxide. By J. M. VAN BEMMELEN (*Rec. Trav. Chim.*, 7, 106—114).—The reddish-brown colloid prepared by adding ammonia to a solution of ferric chloride, contains 6.2 mols. H_2O , after having been kept at 15° in an atmosphere saturated with moisture. After exposure to the air for a year, its composition is constant and it contains 4 to 4.1 mols. H_2O ; in dry air, its composition becomes constant at 1.6 mol. after four months. When heated at 100° in dry air until equilibrium is established, it only contains 0.96 mol. H_2O , but the final composition depends on the state of aggregation. The same sample, after keeping for six years in a closed flask, was heated at temperatures varying from 15° to 150° in dry air and in a saturated atmosphere until the weight was constant; at 15° in dry air, it contained 1 mol. H_2O ; and at 100° , 0.45 mol. H_2O after only five hours. Between 100° and 300° , the reddish-brown colloid decomposes slowly and regularly until the water falls to about 0.25 mol., but if heated sufficiently long at any intermediate temperature the final result is practically the same. When placed in an atmosphere saturated with moisture, after having been heated at temperatures varying from 100° to 300° , it only partially regains the water it has lost; and the higher the temperature to which it has been exposed the greater is the diminution in absorptive power: after having been calcined it absorbs no moisture. This reddish-brown substance is therefore a colloid of variable composition. The yellow colloid prepared by Phillips's method contains 2.43 mols. H_2O when dry, but when kept for a month in a saturated atmosphere it contains 7.4 mols. H_2O . When heated at temperatures increasing from 15° to 270° in a stream of dry air, the water falls from 1.7 to 0.24 mol. Above 200° , its composition is practically the same as that of the reddish-brown colloid at the same temperature; but from about 50° to 300° the former retains water with more energy. F. S. K.

Colloïdal Chromic Oxide. By J. M. VAN BEMMELEN (*Rec. Trav. Chim.*, 7, 114—118).—The bluish colloid, prepared by treating a dilute solution of a chromic salt with ammonia at the ordinary temperature or at 100° , contains originally 11 mols. H_2O ; after exposure to the air at 15° it contains 7.8 to 8 mols., but after keeping for 14 days in an atmosphere saturated with moisture, the quantity of water rises to 13.2 mols., and after exposure to dry air it falls to 7.0 mols. When heated in the air at temperatures increasing from 45° to 200° , the water falls from 5.9 to 2.3 mols., and the colour changes to a dirty green. The results obtained on heating at temperatures varying from 15° to 100° (1) in a saturated atmosphere, (2) in ordinary air,

and (3) in dry air, until the weight is constant, show that at every temperature equilibrium is established between the vapour-tension of the colloïd and that of water at the same temperature. At 65° and at 100°, it retains more water in a saturated atmosphere than at 15° and 65° respectively in a dry atmosphere. After having been heated at from 15° to 100° in dry air, its absorptive power is only slightly diminished, and at higher temperatures it retains more water than colloïdal silica, alumina, stannic acid or ferric oxide at the same temperature, but the higher the temperature to which it has been exposed, the more insoluble it becomes in acids and especially in alkalis. Colloïdal chromic oxide has no definite composition at any temperature between 15 and 280°. F. S. K.

Ultramarine Blue. By F. KNAPP (*J. pr. Chem.* [2], 38, 48—64; compare Abstract, 1887, 110).—When an intimate mixture of equal parts of pure sodium carbonate and flowers of sulphur is heated in a glass tube with a bunsen burner until no more sulphur sublimes, the weight of the residue, from 100 grams of sodium carbonate, is 167.9 grams on the average. If the temperature is raised, the weight remains constant for some time, but at a red heat sulphur again sublimes, and the weight of the residue is 150.6 grams on the average. No further evolution of sulphur occurs even when the mixture is heated with the aid of a blowpipe.

An aqueous solution of liver of sulphur deposits a black precipitate which decomposes in dilute solutions; if this precipitate is washed by decantation as long as the solution is sufficiently concentrated to prevent decomposition, and then boiled with potassium cyanide to free it from ferrous sulphide, it becomes stable, and can be washed with water. This substance is the black modification of sulphur (Magnus), and is the colouring principle of liver of sulphur. When sulphur is gradually added to fused sodium chloride, potassium chloride, or sodium sulphate, and the heating continued until the black turbidity which forms is just dissolved, a bright blue mass is obtained.

The production of ultramarine blue by the method described (*loc. cit.*) is explained as follows:—When liver of sulphur is heated, sulphur is liberated, and, coming in contact with surfaces at a temperature far above its melting point, is converted into the black modification which dissolves in the sodium sulphide and gives to it its greenish tinge. When the sulphide is dissolved in water and the solution brought into contact with calcium phosphate, the black modification is precipitated and the blue produced. Alumina, silica, kaolin, &c., have not sufficient surface attraction until they have become coated with sodium sulphide, so that the blue colour is not formed until the mixture is heated.

Potassium sulphide cannot be employed for the preparation of ultramarine blue, because the black modification of sulphur which is formed does not dissolve but separates at the surface and gets oxidised. F. S. K.

New Method of Forming Alloys. By W. HALLOCK (*Zeit. physikal. Chem.*, 2, 378—379).—The author finds that alloys may be

formed from their components at a temperature below that at which the metal of lowest melting point melts, and without extra pressure, provided the temperature be above the melting point of the alloy itself. An instance of this is Wood's alloy, which is formed from 1 part of cadmium, 1 part of tin, 2 parts of lead, and 4 parts of bismuth; by mixing the metals in the finely-divided state, bringing the mixture into a tube with just sufficient pressure to insure the particles being together, and then heating for some time at 98–100°. Tin and lead may be alloyed by simply laying a clean surface of tin on a clean surface of lead and heating for some hours at 198–200°. The alloy of potassium and sodium which melts above 6° is made by cutting clean surfaces of the metals and pressing them lightly together at the ordinary temperature. H. C.

Astracanite and Hydrated Double Salts. By H. W. B. ROOZEBOOM (*Rec. Trav. Chim.*, 6, 333–355).—The transition points which Van't Hoff has described for the formation or decomposition of astracanite, sodium ammonium racemate, and cupri-calcic acetate, are quintuple points (compare this vol., p. 1152). In the case of astracanite the following phases can coexist at 22°:— $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}(\text{N})$, $\text{MgSO}_4, 7\text{H}_2\text{O}(\text{M})$ astracanite = $\text{Na}_2\text{Mg}(\text{SO}_4)_2, 4\text{H}_2\text{O}(\text{A})$, a solution having the composition $100\text{H}_2\text{O} \approx \frac{4.6\text{MgSO}_4}{2.9\text{Na}_2\text{SO}_4}(\text{L})$ (see below), and aqueous vapour (G). At the quintuple point, there are, therefore, five phases composed of three substances, H_2O , MgSO_4 , and Na_2SO_4 . When heat is supplied to the system, M + N are transformed into A + L. This phenomenon being accompanied by expansion, and the pressure remaining constant as long as the five phases co-exist, part of the aqueous vapour must also dissolve, so that the transformation is expressed thus: $\text{N} + \text{M} + \text{G} \rightleftharpoons \text{A} + \text{L}$; but this equation only gives the symbols of the five phases; in order to express their quantities, the density of the aqueous vapour and of the solution at the quintuple point must be known. The equation shows that the transformation produced by heat will terminate in the disappearance of one of the phases, N, M, G, according to their quantities. From this moment we pass from the quintuple point to higher temperatures with one of the following systems of four phases: A + L + N + M, A + L + N + G, A + L + M + G. This necessitates the existence of three curves for these three complete heterogeneous systems, to the right of the quintuple point. On the other hand, when heat is taken from the system of five phases at the quintuple point, the transformation of A + L into N + M + G may terminate either in the disappearance of A or of L, and there would be two curves for the systems N + M + A + G and N + M + L + G, to the left of the quintuple point. This point is not, therefore, a transition point for only one phase. It is a transition point in the direction ← for the system of two phases, A + L, and these two phases could never exist at any temperature lower than the quintuple point, whereas every other group of two phases amongst M, N, A, L, G could exist on both sides of this point. The quintuple point is also a maximum temperature for the group of phases M + N + G, which could not

exist above this temperature, whereas every other group of three phases amongst N, M, A, L, G could exist on both sides of the quintuple point.

The author discusses, with the aid of diagrams, the case of astracanite and cupri-calcic acetate (compare *Rec. Trav. Chim.*, 6, 91; Abstr., 1888, 401), and arrives at the following conclusions:—

The quintuple point of hydrated double salts is only a limit of temperature for those salts which contain a greater number of molecules of water than their constituent parts, and of which the solution and decomposition into these constituents is accompanied by contraction.

If these two conditions are not both satisfied, the double salt can exist on both sides of the quintuple point in presence of aqueous vapour or of a solution.

A large quantity of astracanite, or of a mixture of the double salt with one of its constituents, was agitated for about three hours in a closed vessel at constant temperature with a quantity of water so small that on standing only a very thin stratum of solution was obtained.

A certain volume of the solution was analysed, and the results are given in the following table:—

Temperature.	Astracanite.		Astracanite + sodium sulphate.		Astracanite + magnesium sulphate.	
	Na ₂ SO ₄ .	MgSO ₄ .	Na ₂ SO ₄ .	MgSO ₄ .	Na ₂ SO ₄ .	MgSO ₄ .
18.5°	—	—	—	—	3.41	4.27
22.0	2.95	4.70	2.95	4.70	2.85	4.63
24.5	{ 3.44	3.70	{ 3.45	3.62	{ 2.75	4.71
	{ 3.46	3.66			{ 2.62	4.81
30.0	{ 3.60	3.60	{ 4.58	2.91	2.30	5.31
	{ 3.59	3.59				
35.0	{ 3.69	3.69	{ 4.30	2.76	{ 1.75	5.89
	{ 3.74	3.74			{ 1.71	5.87
47.0	3.60	3.60	—	—	—	—

From the diagram which is given, showing the curves of solubility at various temperatures, it is seen that above 25° a solution prepared from astracanite and an excess of sodium sulphate contains a greater number of molecules of sodium sulphate than of magnesium sulphate, but below 25°, even in the presence of Na₂SO₄.10H₂O, a solution is obtained containing a larger number of molecules of magnesium sulphate than of sodium sulphate. It is evident, therefore, that if the pure double salt is placed in contact with water it will be partially decomposed, and Na₂SO₄.10H₂O will separate until equilibrium is established. The lower the temperature, the greater will be the decomposition, until at 22° the same solution is obtained from pure astracanite and from a mixture of the double salt and sodium sulphate.

A saturated solution of astracanite and magnesium sulphate always

contains a larger number of molecules of magnesium sulphate than of sodium sulphate, so that such a solution can never be obtained from astracanite alone. The values obtained at 18.5° with a solution prepared from astracanite and magnesium sulphate show that, if the double salt could be kept from decomposing at still lower temperatures, at about 15° , a solution would be obtained containing an equal number of molecules of the two sulphates. At 22° , the double salt could exist in presence of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ at the bottom of a solution containing 4.65 MgSO_4 and $2.9 \text{ Na}_2\text{SO}_4$ in $100 \text{ H}_2\text{O}$. It is this solution which exists at the quintuple point (see above). At 17.9° , the solution contains $2.12 \text{ Na}_2\text{SO}_4$ and 4.56 MgSO_4 , at 18.5° $2.16 \text{ Na}_2\text{SO}_4$ and 4.59 MgSO_4 (compare Van't Hoff, *Rec. Trav. Chim.*, **5**, 259, and Diacon, *Jahrsb.*, 1866, 64). At the transition point (22°) for the double salt in presence of a solution, the solubility is the same for each of the three systems: astracanite + MgSO_4 , astracanite + Na_2SO_4 , and Na_2SO_4 + MgSO_4 .

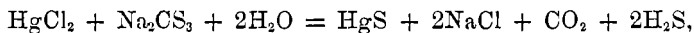
At temperatures above 25° , astracanite, placed in contact with water, dissolves without either of the simple salts separating, because the solution which is obtained in presence of either constituent contains a larger quantity of this constituent than is present in the double salt. From 25° to 47° , the solubility of astracanite hardly varies at all with the temperature.

The relation between the molecular quantities of sodium sulphate and magnesium sulphate in the different solutions which can exist in equilibrium with the double salt between 22° and 35° (?) can probably be expressed very closely by the formula $C_{\text{MgSO}_4} \times C_{\text{Na}_2\text{SO}_4} = K$. This product varies very slightly with the temperature.

Two facts of general importance result from this investigation, namely—(1) There are two limits of composition for the solution which can exist in equilibrium with a double salt. These limits are reached when the liquid is placed in contact with the double salt and with each of its constituents. (2) There is a limit of temperature above or below which the double salt is either decomposed or not by the solvent.

F. S. K.

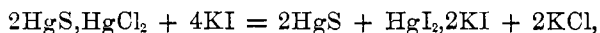
Chlorosulphides of Mercury. By T. POLECK and C. GOERCKI (*Ber.*, **21**, 2412—2417).—When chlorine is passed into water containing freshly precipitated mercuric sulphide, the latter becomes bright yellow, and finally dissolves. The bright yellow substance has the composition $2\text{HgS}, \text{HgCl}_2$ (compare Rose, *Ann. Phys. Chem.*, **13**, 59). When solutions of sodium thiocarbonate and mercuric sulphide are mixed, the following reaction takes place:—



but if a large excess of dry mercuric chloride is treated with a solution of sodium thiocarbonate, the product has the composition $2\text{HgS}, \text{HgCl}_2$. This same substance is formed when a solution of mercuric chloride (2 mols.) is precipitated with a solution of sodium thiosulphate (1 mol.).

When mercuric sulphide (1 mol.) is treated with a solution of mercuric chloride (1 mol.), half of the latter remains in solution,

whereas when 2, 3, 4, or 5 mols. of the sulphide are present the solution contains no chloride, and bright yellow products are formed, the compositions of which are $2\text{HgS}, \text{HgCl}_2$, $3\text{HgS}, \text{HgCl}_2$, and $4\text{HgS}, \text{HgCl}_2$ respectively. These products are all insoluble in hydrochloric acid, nitric acid, and water, but are blackened and decomposed by potash. They can also be obtained by boiling a solution of mercuric chloride (1 mol.) with 2, 3, and 4, mols. of the sulphide. They are not by boiling with a concentrated solution of changed sodium chloride, but at 190° they are converted into their constituents. When heated at 170° with a solution of potassium iodide, the substance $2\text{HgS}, \text{HgCl}_2$ is decomposed according to the equation—



and the other products behave similarly. In all cases, the red modification of mercuric sulphide is obtained, which fact the authors consider is a proof that these products are true compounds.

Freshly precipitated mercuric sulphide is not converted into the red modification when treated in the same way, nor is the product obtained by precipitating mercuric chloride with sodium thiosulphate.

F. S. K.

Organic Chemistry.

Formation and Decomposition of Ethereal Salts: Compounds of Amylene (Trimethylethylene) with Acids as Cases of Chemical Equilibrium. By D. KONOWALOFF (*Zeit. physikal. Chem.*, 2, 380—389).—The compounds of amylene with acetic acid and its chloro-derivatives, as has already been shown (this vol., p. 340), undergo decomposition when heated in the presence of any of the free acid, although otherwise stable. The decomposition is limited by the amount of free acid present, the temperature, and the time of heating. On the other hand, from experiments with the dichloroacetate, it would appear that the presence of excess of the acid is more favourable to the formation of the salt than the presence of excess of the amylene, which appears rather to retard the reaction. This retardation caused by the excess of amylene present, is, as the author thinks, due to a change in the condition of the acid which the amylene affects. Such a change would be similar to that observed by Raoult in acetic acid, the molecular weight of which, when determined by the lowering of the freezing point, is double in benzene what it is in formic acid. This is supported by the fact that if trichloroacetic acid be treated with excess of amylene, the formation of the salt takes place more readily on the addition of benzene to the solution, and that with a large quantity of benzene present the conditions of the reaction are very nearly those required by the law of mass action.

H. C.

The Hydrocarbons C_8H_{16} and C_9H_{18} obtained from Methyl Dipropyl Carbinol and Ethyl Dipropyl Carbinol. By E. SOKOLOFF (*J. Russ. Chem. Soc.*, 1887, 599—601).—The hydrocarbon C_8H_{16} was obtained when methyl dipropyl carbinol was prepared from methyl iodide, zinc, and butyrene. It is a light, mobile liquid, boiling at 120.4° (corr.), and having the sp. gr. 0.73138 at 20° ; 0.72287 at 30° ; and 0.71746 at 35° . The bromide is $C_8H_{16}Br_2$. The products of oxidation are propionic and acetic acids. The probable constitution is $CMePr:CHEt$. The hydrocarbon, C_9H_{18} , was obtained from the iodide of ethyl propyl carbonyl and alcoholic potash. It boils at 138° , and has the sp. gr. 0.74333 at 20° ; 0.74344 at 30° ; and 0.72990 at 35° .

B. B.

Isomeric Change of Disubstituted Acetylenes and of Dimethylallene under the Influence of Metallic Sodium: Synthesis of Acetylenecarboxylic Acids. By A. FAVORSKY (*J. Russ. Chem. Soc.*, 1887, 553—565).—Disubstituted acetylenes are usually said to be distinguished from their monosubstituted isomerides containing the acetylene group $CH:C$, by not yielding copper and silver compounds, as the latter do, and by not uniting with the alkali metals. The author finds that this is not strictly accurate, as the disubstituted acetylenes unite easily with sodium, forming metallic derivatives, which are usually obtained in the form of white powders. When treated with alcohol or water, these compounds yield oily substances, which have the odour and other properties of monosubstituted acetylenes, forming characteristic copper and silver compounds, and yielding the corresponding ketones on treatment with sulphuric acid. The author has examined the question whether the intramolecular or isomeric transformation takes place when the sodium acts on the hydrocarbon or when the sodium compound is decomposed by alcohol or water. In the first place, the sodium-derivatives were investigated in the case of methylethylacetylene, methylpropylacetylene, and dimethylallene.

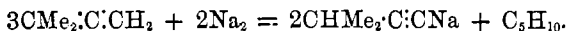
Methylethylacetylene was sealed up with slightly less than its equivalent of sodium in a tube, and heated at 100° . The complete formation of the sodium compound takes place easily, and no pressure was observed on opening the tube. The product was washed with ether, and decomposed by water, when propylacetylene was formed; this gives precipitates with ammoniacal solutions of copper and silver nitrates. On heating it in sealed tubes with mercuric chloride, methyl propyl ketone is obtained. In order to ascertain the constitution of the sodium compound it was mixed with ether and dry carbonic anhydride was passed over it for a day, when it was found to be converted into the sodium salt of a carboxylic acid. The acid itself, set free by means of dilute sulphuric acid, forms feathery crystals melting at 27° , and distilling only under reduced pressure (at 125° and 20 mm.). It is deliquescent, although not easily soluble in water, but easily soluble in alcohol, ether, and light petroleum. The vapour-density of the acid could not be determined, as on boiling it is decomposed into propylacetylene and carbonic anhydride. Its composition is $CH_2Me:CH_2C:C:COOH$, and the following salts are described:— $C_8H_7NaO_2$; $(C_8H_7O_2)_2Ba + 3H_2O$; $(C_8H_7O_2)_2Ca$; $(C_8H_7O_2)_2Cu + 2H_2O$.

The silver salt could not be obtained. On acting with silver nitrate on the ammonium salt, a decomposition of the precipitate first formed takes place, carbonic anhydride being produced, together with the silver compound of valerylene, which yields propylacetylene when treated with weak hydrochloric acid. The acid is therefore *propylacetylenecarboxylic acid*, and the original sodium compound has the constitution $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{C}:\text{CNa}$. The formation of this latter without evolution of hydrogen may be explained by the following equation:—
 $3\text{CH}_2\text{Me}\cdot\text{C}:\text{CMe} + 2\text{Na} = 2\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{C}:\text{CNa} + \text{CH}_2\text{Me}\cdot\text{CH}:\text{CHMe}.$

Dimethylallene under similar circumstances yields a sodium-derivative, which on decomposition with water gives isopropylacetylene. The sodium compound is converted by carbonic anhydride into a sodium salt, from which *isopropylacetylenecarboxylic acid*,



was obtained. The calcium, barium, and copper salts are described. Instead of the silver salt, valerylene silver was formed, as in the case of the propyl-derivative; this gave isopropylacetylene on treatment with weak hydrochloric acid. The acid melts at 38° , and boils at $106\text{--}107^\circ$ under 20 mm. pressure. The constitution and formation of the sodium compound may be represented as follows:—



The sodium compound of *methylpropylacetylene* was prepared by heating the hydrocarbons with sodium at $150\text{--}160^\circ$. When treated with water, it gives butylacetylene and carbonic anhydride. *Butylacetylenecarboxylic acid*, $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}:\text{C}\cdot\text{COOH}$, is a liquid which boils at 135° under 20 mm. pressure, and does not solidify at -20° . The barium and calcium salts are described. The silver salt is a little more stable than the salts of the acids previously mentioned, but after a time it decomposes in a similar manner. The change is analogous to those described above: $3\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{C}:\text{CMe} + 2\text{Na} = \text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}:\text{CNa} + \text{C}_6\text{H}_{12}$. Under the influence of alcoholic alkalis, monosubstituted acetylenes are, as the author has found (this vol., p. 798), converted into the disubstituted ones, whereas the reverse reaction is now shown to take place under the influence of sodium. In this process the formation of any intermediate compounds cannot be assumed, and the reaction may therefore be regarded as a typical case of a change of the position of atoms within the molecule.

B. B.

Methyl Chlorothioformate: Polymeric Thiocarbonyl Chloride. By B. RATHKE (*Ber.*, 21, 2539—2545).—The polymeride obtained by exposing thiocarbonyl chloride to light melts at 116° (not 112.5°). When the solution in benzene is heated in a water-bath with aniline, the compound $\text{S} \begin{smallmatrix} \text{CCl}_2 \\ \text{CS} \end{smallmatrix} \text{NPh}$ is formed. This crystallises in lustrous, rhombic plates, melts at 69.5° , and is readily soluble in the usual organic solvents. When the polymeride is heated with 3 mols. of aniline dissolved in benzene, for half an hour, and then again with the same amount of aniline, phenylthiocarbimide, diphenylthiocarbamide, and the hydrochlorides of aniline and tri-

phenylguanidine are formed. These reactions make it probable that the polymeride has the constitution $\text{CSCl}\cdot\text{S}\cdot\text{CCl}_3$. This is confirmed by the similar properties of the corresponding oxygen-derivative, methyl perchloroformate (Hentschel, Abstr., 1887, 1027 and 1099).

The compound $\text{C}_2\text{S}_2\text{Cl}_4$ is converted by aqueous ammonia into ammonium thiocyanate and chloride. It is decomposed by cold alcohol, with formation of an oil. N. H. M.

Action of Methyl Iodide and Zinc on Ethyl Propyl Ketone.

By E. SOKOLOFF (*J. Russ. Chem. Soc.*, 1887, 587—595).—For the investigation of Saytzeff's reaction in the case of mixed ketones, ethyl propyl ketone was mixed with methyl iodide and finely granulated zinc added. After standing for 11 days in water at the ordinary temperature, the mixture was heated for three days on a water-bath. *Methyl ethyl propyl carbinol*, $\text{CMeEtPr}\cdot\text{OH}$, was obtained as an aromatic liquid boiling at $140\cdot3^\circ$, and having a sp. gr. of $0\cdot8234$ at 20° and $0\cdot8106$ at 35° . On heating it with acetic anhydride at 140° , the acetate, $\text{CMeEtPr}\cdot\text{OAc}$, boiling at 158 — 159° , was obtained.

Chromic acid oxidises the alcohol to propionic and acetic acids, carbonic anhydride, some ethyl propyl ketone being formed at the same time, together with a small quantity of a hydrocarbon, C_7H_{14} , boiling at $97\cdot4^\circ$, and having the sp. gr. $0\cdot71812$ at 20° , $0\cdot70879$ at 30° , and $0\cdot70535$ at 35° . It yields the bromide, $\text{C}_7\text{H}_{14}\text{Br}_2$, and the iodide, $\text{C}_7\text{H}_{14}\text{I}_2$. The coefficient of refraction found corresponds with one double union in the hydrocarbon. On oxidising this hydrocarbon with chromic mixture, propionic and acetic acids were obtained without any ketone; its constitution, therefore, remains undetermined.

B. B.

Action of Ethyl Iodide and Zinc on Ethyl Propyl Ketone.

By E. SOKOLOFF (*J. Russ. Chem. Soc.*, 1887, 595—598).—The method employed was the same as that described in the former paper (preceding Abstract). *Diethyl propyl carbinol*, $\text{CEtPr}\cdot\text{OH}$, was obtained, boiling at $160\cdot5^\circ$, and having the sp. gr. $0\cdot83794$ at 20° , $0\cdot83008$ at 30° , and $0\cdot82615^\circ$ at 35° . The acetate boils at 176 — 178° . The carbinol, when oxidised, yields butyric, propionic, and acetic acids. An unsaturated hydrocarbon, C_8H_{16} , is formed at the same time; this boils at $118\cdot5^\circ$, and has the sp. gr. $0\cdot73465$ at 20° , $0\cdot72598$ at 30° , and $0\cdot72034$ at 35° . The bromide is $\text{C}_8\text{H}_{16}\text{Br}_2$. The oxidation products of the hydrocarbon are butyric, propionic, and acetic acids. Constitution unknown.

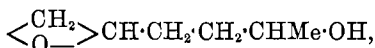
B. B.

Butallyl Methyl Pinacone. By I. KABLUKOFF (*J. Russ. Chem. Soc.*, 1887, 513—516).—This is obtained as a bye-product in the preparation of butallyl methyl carbinol by Crow's method from allyl acetone, addition of hydrogen taking place. Its formula is $\text{C}_{12}\text{H}_{22}\text{O}_2$, or $\text{C}_3\text{H}_5\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{C}_3\text{H}_5$. It is an oily liquid boiling at 180 — 182° (74 mm. pressure), or with partial decomposition at $264\cdot5$ — $266\cdot5^\circ$ (760 mm.). Its sp. gr. is $0\cdot9632$ at 0° , and $0\cdot9452$ at 24° . The coefficient of dilatation between 0° and 24° is $0\cdot0008238$. By the action of bromine, the compound $\text{C}_{12}\text{H}_{22}\text{Br}_2\text{O}_2$, is formed: an additive compound corresponding with the saturation of

the two allyl-groups. On oxidation with potassium permanganate in alkaline solution, ethyl acetate is regenerated, the analogy with pinacone being thus shown. B. B.

Derivatives of Hexyl Glycerol (Hydrated Butallyl Methyl Carbinol Oxide). By I. KABLUKOFF (*J. Russ. Chem. Soc.*, 1887, 502—513).—This glycerol was described by Markownikoff and the author in 1880 as the first homologue of glycerol in the fatty series. Before giving an account of some of its derivatives, the author proposes a new nomenclature for glycerols, the possible number of isomerides of glycerol with six carbon-atoms, for instance, being more than 20. The name of a glycerol is derived from the name of the unsaturated alcohol from which it is obtained, whilst the glycides are regarded as the oxides of these alcohols, and the glycerols as their hydrates.

The glycerol in question corresponds with butallyl methyl carbinol, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$; its oxide is

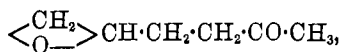


and the hydrate of this oxide, $\text{CH}_2(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, is hexyl glycerol.

Hexyl Glyceryl Ketone.—In order to prepare this hexyl ketone, sodium is dissolved in alcohol and ethyl acetoacetate and epichlorhydrin added. After heating the mixture on the water-bath, the sodium chloride is removed by filtration, the alcohol distilled off under diminished pressure, and water is added, when an oily layer separates at the bottom of the aqueous liquid; by agitating the aqueous liquid with ether, a further quantity of the oil may be extracted. This oil was saponified with baryta, and the excess of the latter separated by passing in carbonic anhydride. After evaporation on the water-bath, a thick, oily liquid was obtained, from which some baryta salt separated on the addition of absolute alcohol, and the alcoholic extract yielded the ketone of hexyl glycerol, $\text{C}_6\text{H}_{10}\text{O}(\text{OH})_2$. This boils at $170\text{--}180^\circ$ under a pressure of 15 mm., but was not further investigated.

The Monochlorhydrin of Hexyl Glycerol.—This may be prepared by Eltekoff's method, namely, the action of aqueous hypochlorous acid on butallyl methyl carbinol, but as the yield is very small, only a small part of the carbinol entering into reaction, Lauch's method (*Abstr.*, 1885, 1194) is to be preferred. For this purpose, the carbinol (10 grams) is mixed with a saturated solution of boric acid (200 c.c.) and a solution of bleaching powder gradually added. After standing in the dark for 24 hours, the product is extracted with ether, when the chlorhydrin, $\text{C}_6\text{H}_{13}\text{ClO}_2$, is obtained (5.5 grams). It can be distilled under reduced pressure, but under atmospheric pressure (at 180°) it is decomposed into the glycide and hydrochloric acid. The *monochlorhydrinacetin* is obtained on addition of hypochlorous acid to butallyl methyl carbinol acetate and extraction with ether. It can be distilled only under reduced pressure, when it boils at $172\text{--}176^\circ$ (50 mm.).

The Glycide of Hexyl Alcohol (Butallyl Methyl Carbinyl Oxide).—This is formed by the action of potassium hydroxide (2 mols.) on the monochlorhydrinacetin at a gentle heat. It is a light, mobile liquid of sp. gr. 1.0099 at 21°, boiling at 178–181°. It has the formula $\langle \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix} \rangle \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{OH}$, but it cannot be got quite free from chlorine compounds. It is not altered by heating with water at 115° for 44 hours. The author did not succeed in adding the elements of hydrogen chloride to the glycide so as to convert it into the monochlorhydrin. In order to obtain the ketone of the glycerol, $\text{C}_6\text{H}_{11}(\text{OH})_2\text{O}$, allylacetone is treated with hypochlorous acid. The product is saponified with baryta, the excess of the latter removed by carbonic anhydride, and after removing the barium carbonate by filtration, the liquid is evaporated on the water-bath. The residue is then extracted with alcohol, and the alcoholic extract evaporated, when a liquid is obtained which may be distilled under reduced pressure. The oil thus obtained has the formula



that is, it is the oxide of allylacetone, the expected ketone.

B. B.

Action of Polyatomic Alcohols on Solutions of Boric Acid and Hydrogen Sodium Carbonate. By C. JEHN (*Arch. Pharm.* [3], 26, 495–497; compare Abstract, 1887, 790).—Sulzer has found that solutions of boric acid or borax and normal sodium carbonate react on each other on the addition of glycerol and honey (glucose), provided the boric acid or borax solution be added in considerable excess. The author confirms the above, and finds further that chemically pure lævulose causes reactions in solutions of NaHCO_3 and H_3BO_3 , in NaHCO_3 and $\text{Na}_2\text{B}_4\text{O}_7$, and in Na_2CO_3 and H_3BO_3 (in this case under Sulzer's conditions, when mannitol also is effective). Solutions of borax and normal sodium carbonate do not react either on addition of lævulose or mannitol. The alcohol dulcitol (melampyrit), $\text{C}_6\text{H}_8(\text{OH})_6$, and the aldehydes lævulose and lactose cause the reaction. The alcohol quercitol, $\text{C}_6\text{H}_7(\text{OH})_6$, does not influence the mixed solutions. The author concludes that the reaction is caused by those polyatomic alcohols and corresponding aldehydes only where their molecules contain as many hydroxyl-groups as carbon-atoms.

J. T.

Propylenediamine and Trimethylenediamine. By H. STRACHE (*Ber.*, 21, 2358–2369).—Propylenediamine hydrochloride melts at 220° (compare Hofmann, *Ber.*, 6, 308).

A compound, $\text{C}_3\text{H}_{14}\text{N}_2 + \text{H}_2\text{O}$, is contained in the higher boiling portions of the product obtained by the action of propylene bromide on alcoholic ammonia. It is a slightly yellow, mobile oil, boils at 203–207°, and is miscible with water, alcohol, and benzene in all proportions. It is not decomposed by alkalis or chromic acid, and it combines readily with methyl iodide.

Diacetylpropylenediamine, $\text{C}_3\text{H}_8(\text{NHAc})_2$, prepared by adding an

excess of acetic anhydride to aqueous propylenediamine, crystallises from alcoholic benzene in white, deliquescent needles, melts at $138-139^{\circ}$, and is readily soluble in water, alcohol, and chloroform, sparingly in benzene, and insoluble in ether and light petroleum.

Dibenzoylpropylenediamine, $C_3H_6(NHBz)_2$, prepared by heating a mixture of benzoic chloride and aqueous propylenediamine, separates from benzene in colourless, granular crystals, melts at $192-193^{\circ}$, is readily soluble in alcohol and hot benzene, sparingly in ether and cold benzene, and insoluble in water.

A mixture of *propyleneoxamide*, $C_3H_6<\begin{smallmatrix} NH\cdot CO \\ NH\cdot CO \end{smallmatrix}>$, and *propylene-oxamic acid*, $NH_2\cdot C_3H_6\cdot NH\cdot CO\cdot COOH$, is obtained when the diamine is mixed with methyl oxalate in alcoholic solution. When the mixture is boiled for a long time with water, the amide is completely converted into the acid. The latter is a white, seemingly amorphous substance, almost insoluble in ordinary solvents, but rather less sparingly soluble in alcohol than the amide.

Propylenesuccinimide, $C_2H_4<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>N\cdot C_3H_6\cdot N<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>C_2H_4$, is obtained when the diamine (1 mol.) is heated with succinic anhydride (1 mol.) at $150-160^{\circ}$. It crystallises from benzene, melts at $98-100^{\circ}$, and is decomposed by boiling baryta water or warm sulphuric acid.

Dibenzylidenepropylenediamine, $C_3H_6(N\cdot CHPh)_2$, prepared by mixing the diamine with benzaldehyde, is a yellowish oil which cannot be distilled; it is miscible with alcohol, ether, and benzene in all proportions, but is insoluble in water, and is decomposed by mineral acids. Acetophenone and the diamine react at 200° , yielding a red oil, $C_3H_6(N\cdot CMePh)_2$, which distils at $350-370^{\circ}$.

Ethyl propylene- β -amido- α -crotonate, $C_3H_6(NH\cdot CMe\cdot CH\cdot COOEt)_2$, obtained by the action of ethyl acetoacetate on propylenediamine, is a brownish oil. It is readily soluble in ether, alcohol, and benzene, but insoluble in water, and is decomposed by mineral acids.

A condensation product, probably $\begin{array}{c} C_6H_4\cdot C\cdot N\cdot CMe \\ | \quad || \quad | \\ C_6H_4\cdot C\cdot N\cdot CH \end{array}$, is formed when

aqueous propylenediamine is added to a boiling alcoholic solution of phenanthraquinone. It crystallises from alcohol in white, flexible needles, melts at $127-128^{\circ}$, is readily soluble in benzene, chloroform, and hot alcohol, moderately soluble in cold alcohol and ether, and insoluble in water. The *hydrochloride* crystallises in needles, and is decomposed by water and alcohol or when exposed to the air. The base separates unchanged from hot concentrated nitric acid, and is precipitated unchanged when water is added to a concentrated sulphuric acid solution. It is decomposed when heated at 200° with concentrated sulphuric acid, and is partially oxidised by chromic acid in acetic acid solution. The *platinochloride*, $(C_{17}H_{12}N_2)_2\cdot H_2PtCl_6$, is unstable, very hygroscopic, and decomposes when heated at 200° without melting.

The compound $CPh<\begin{smallmatrix} CPh\cdot N \\ N\cdot CH_2 \end{smallmatrix}>CHMe$ is the condensation product

of the diamine and benzil. It crystallises in slender needles, melts at 111–112°, and is readily soluble in benzene, chloroform, and hot alcohol, moderately soluble in cold alcohol and ether, rather sparingly in light petroleum, and insoluble in water. It is decomposed by acids.

The compound $2C_6H_{14}N_2 + H_2O$ is obtained as a bye-product in the preparation of trimethylenediamine from the bromide. It crystallises in brownish-yellow, deliquescent needles, melts below 25°, and boils considerably above 350°. It has a somewhat ammoniacal smell, and is readily soluble in all solvents. The hydrochloride and the sulphate are white, crystalline, deliquescent salts.

Diacetyltrimethylenediamine, $C_8H_{16}(NHAc)_2$, prepared by gradually adding acetic anhydride to the diamine and boiling the mixture, crystallises from alcohol in slightly coloured, concentrically grouped needles, melts at 79°, is readily soluble in water, alcohol, and chloroform, moderately so in benzene, but insoluble in ether and light petroleum.

Dibenzoyltrimethylenediamine, $C_{18}H_{20}(NHBz)_2$, prepared in like manner from the diamine and benzoic chloride, separates from benzene in the form of a white, crystalline powder, melts at 147–149°, is readily soluble in alcohol and chloroform, moderately so in hot benzene, and insoluble in water.

Trimethylenoxamide, $C_3H_8(NH)_2C_2O_2$, is obtained mixed with the amic acid when the diamine is treated with methyl oxalate in alcoholic solution. It is a white, amorphous powder, does not melt at 250°, is very sparingly soluble in boiling water, and insoluble in other solvents.

Trimethylenediamine condenses with benzaldehyde, forming a compound, $C_9H_{12}(N:CHPh)_2$, and with acetophenone yielding the compound $C_9H_{12}(N:CPhMe)_2$. Both products are oils which cannot be distilled, and are insoluble in water, but readily soluble in other solvents.

The condensation product of the diamine with phenanthraquinone is a yellow, crystalline powder, which has the composition $C_{26}H_{17}NO_2$. It is insoluble in water, sparingly soluble in alcohol and ether, moderately in benzene, and does not melt when heated at 250°.

The compound $CH_2 < \begin{smallmatrix} CH_2 \cdot N : CPh \\ CH_2 \cdot N : CPh \end{smallmatrix} >$ is formed when benzil and the diamine are heated together at 110° with a little alcohol. It is a reddish-brown, vitreous substance, which softens at 72°, melts completely at 80°, and is readily soluble in ordinary solvents.

F. S. K.

Septdecylamine. By G. S. TURPIN (*Ber.*, **21**, 2486–2492).—Septdecylamine is best prepared by distilling septdecylstearylcarbamide with lime; stearone is formed in the reaction. The product is dissolved in alcohol, filtered from undissolved stearone, and evaporated with hydrochloric acid. The crystalline hydrochloride which separates is washed with pure ether, dissolved in a little hot alcohol, and precipitated with ether. The free base melts at 49°, boils at about 335–340°, dissolves in alcohol and ether, and readily attracts moisture and carbonic anhydride from the air. The hydrochloride crystallises from alcohol in plates of a fatty lustre. The

benzoyl-derivative, $\text{NHBz}\cdot\text{C}_{17}\text{H}_{35}$, forms plates of a fatty lustre and melts at 91° .

Septdecylamine septdecyldithiocarbamate, $\text{C}_{35}\text{H}_{74}\text{N}_2\text{S}_2$, prepared by mixing an ethereal solution of the amine with carbon bisulphide, is a lustrous powder melting at 90° with decomposition. When boiled with alcohol, *diseptdecylthiocarbamide*, $\text{C}_{35}\text{H}_{72}\text{N}_2\text{S}$, melting at 94° is formed.

Septdecylthiocarbimide, $\text{C}_{18}\text{H}_{35}\text{NS}$, is formed together with a small amount of *diseptdecylthiocarbamide* when the amine is heated with alcohol and carbon bisulphide on a water-bath. It melts at 32° , dissolves readily in alcohol and ether, and does not distil without decomposition. When heated with alcoholic ammonia at 100° , *monoseptdecylthiocarbamide*, melting at 110 – 111° , is formed. *Phenylseptdecylthiocarbamide*, $\text{C}_{24}\text{H}_{42}\text{N}_2\text{S}$, obtained by boiling the isothiocyanato with alcohol and aniline, melts at 79° .

Diseptdecylcarbamide, $\text{C}_{35}\text{H}_{72}\text{N}_2\text{O}$, prepared by treating the corresponding thiocarbamide with mercuric oxide, is sparingly soluble and melts at 75° .

Monoseptdecylcarbamide, $\text{C}_{18}\text{H}_{35}\text{N}_2\text{O}$, is obtained by evaporating the alcoholic solution of septdecylamine hydrochloride and potassium cyanate, and extracting the residue with absolute alcohol; it melts at 109° .

The *isocyanate* is formed as an oil when the hydrochloride is heated with a solution of carbonyl chloride in benzene at 100° . When boiled with absolute alcohol, *septdecylurethane*, $\text{C}_{20}\text{H}_{41}\text{NO}_2$, is obtained. This crystallises in lustrous plates and melts at 62° .

Phenylseptdecylcarbamide, $\text{C}_{24}\text{H}_{42}\text{N}_2\text{O}$, obtained by evaporating the thiocarbamide with a solution of aniline in benzene, crystallises in slender, lustrous needles melting at 99° . N. H. M.

Condensation of Glyoxal with Ethyl Acetoacetate. By M. POLONOWSKY (*Ber.*, **21**, 2499–2500).—An answer to Fittig and Schloesser (this vol., p. 1089).

Sulphacetic Acid and its Derivatives. By A. P. N. FRANCHIMONT (*Rec. Trav. Chim.*, **7**, 25–33).—Sulphopropionic acid and sulphobutyric acid can be readily prepared by the same method as that employed in the case of sulphacetic acid (compare Franchimont, *Compt. rend.*, **92**, 1054). Sulphacetic acid melts at about 75° , loses its water at about 160° , and at about 230° carbonic anhydride (about 1 mol. from 2 mols. acid) is evolved and acetic acid distils, but sulphurous anhydride and carbon are always produced in small quantities. Sulphacetic acid does not yield a nitro-derivative when the free acid or the anhydrous barium salt is heated with nitric acid. *Calcium sulphacetate* dried at 240° contains 1 mol. H_2O . The silver salt crystallises in shining plates or in prisms.

Diethyl sulphacetate can be obtained by treating the finely divided silver salt with ethyl iodide. It is sparingly soluble in water and boils at a high temperature, but undergoes decomposition. At the same time a crystalline salt, $\text{C}_6\text{H}_{14}\text{Ag}_2\text{S}_3\text{O}_{16}$, is formed in the preparation of diethyl sulphacetate by the above method, and remains when

the reaction product is extracted with ether. It dissolves in water, forming a strongly acid solution from which the normal salt crystallises. The normal salt is also formed when the acid salt is kept on blotting paper in a moist atmosphere.

Sulphobutyric acid is produced in small quantity, together with other compounds, when ethyl sulphacetate is treated with alcoholic sodic ethoxide and ethyl iodide.

F. S. K.

Action of Sodium on Ethyl Butyrate and Isobutyrate. By R. BRÜGGEMANN (*Annalen*, **246**, 129—160).—The products of the action of sodium on the ethyl salt of normal butyric acid are sodium ethylenebutylenebutyrate, $C_3H_3(C_2H_4)(C_4H_9) \cdot COONa$, ethylbutyric acid, ethylenebutyric acid, ethylenebutylenedibutyric acid, $C_4H_2O_4$, dibutylenedibutyric acid, $C_{16}H_{28}O_4$, ethylenedibutylenedipropyl ketone, $C_{17}H_{28}O$, and small quantities of dipropyl ketone, ethylenedipropyl, and ethylenebutylenedipropyl ketones. No acid containing three oxygen-atoms is formed.

The chief products of the action of sodium on ethyl isobutyrate are isobutylisobutyric acid and di-isobutyronone. Ethylisobutyric, ethyleneisobutyric, and isobutylene-isobutyric acids are probably formed in small quantities. *Isobutylisobutyric* acid melts at 18° and boils at 215° . *Di-isobutyronone*, $C_3H_7 \cdot CO \cdot C_3H_5 \cdot C_3H_5 \cdot CO \cdot C_3H_7$, boils at 264 — 268° .

Wohlbrück (*Ber.*, **20**, 2332) states that the ethylic salt of isobutyroisobutyric acid, $C_6H_{14}O_3$, and the sodium salt of hydroxycaprylic acid, $C_8H_{16}O_3$, are formed by the action of sodium on ethyl isobutyrate mixed with ether. The author proves that the products of the reaction are the ethylic salts of isobutylisobutyric and ethylisobutyric acids, the sodium salts of isobutylene-isobutyric and ethylene-isobutyric acids and ketones.

W. C. W.

Alloisomerism in the Crotonic Acid Series. By A. MICHAEL and H. PENDLETON (*J. pr. Chem.* [2], **38**, 1—5).—Compare Michael and Norton, *Amer. Chem. J.*, **2**, 15; Erlenmeyer and Müller, *Ber.*, **15**, 49.

When α -bromocrotonic acid, melting at 92° , is heated at 130 — 140° in sealed tubes for 15 hours, it undergoes intramolecular change, and is wholly converted into bromocrotonic acid melting at 106° . By treating this acid (m. p. 106°) with bromine in carbon bisulphide solution, it is converted into an α - β -tribromobutyric acid, melting at 115.5 — 116° , and identical with that obtained from allo- α -bromocrotonic acid. The yield is theoretical. *Barium α - β -tribromobutyrate* crystallises with 1 mol. H_2O and is readily soluble in water. α - β -Tribromobutyric acid loses hydrogen bromide when treated with cold alcoholic potash and is converted into α - β -dibromocrotonic acid, melting at 94° , and identical with the acid obtained by Pinner (*Ber.*, **14**, 1081) by brominating tetrolic acid. The *potassium* salt of this acid is anhydrous and readily soluble in water. The *barium* salt crystallises in prisms with $3\frac{1}{2}$ mols. H_2O , and is readily soluble in water.

These results prove that the bromine is in the α -position in both monobromocrotonic acids.

Sarnow (*Ann.*, **164**, 197) has shown that solid crotonic acid is

obtained when α -chlorocrotonic acid, melting at 97° , is reduced. The corresponding bromocrotonic acid (m. p. 106°) yields solid crotonic acid when treated with sodium amalgam, but the bromocrotonic acid melting at 92° also gives the solid acid when treated similarly, and under varying conditions so as to exclude the possibility of any secondary reaction taking place. The yield is theoretical.

It seems, therefore, that both acids are derived from solid crotonic acid.

The monobromocrotonic acids behave very differently when warmed with dilute potash; the acid melting at 106° loses 1 mol. HBr in a very short time, whereas, that melting at 92° only loses a small quantity of hydrogen bromide in the same time, and even after heating for several hours the change is not complete.

α -Chlorocrotonic acid, melting at 67° , is converted into the alloisomeric α -chlorocrotonic acid, melting at 97° , when heated for 12 hours at 150 – 160° , and bromomaleic acid is converted into bromofumaric acid when treated in like manner.

The results of these experiments may be summarised as follows:—When two unsaturated monobromo-acids are formed from one α - β -dibromo-acid, they are alloisomeric. If two alloisomeric α -halogen acids exist, the one with the lower melting point can be converted into the acid of higher melting point by heating. The acid of higher melting point loses hydrogen bromide more readily than that of lower melting point.

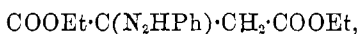
F. S. K.

Action of Hypochlorous Acid on Angelic Acid. By P. MELIKOFF (*J. Russ. Chem. Soc.*, 1887, 524–529).—In a former paper, the author studied the action of hypochlorous acid on isocrotonic acid and obtained two chlorisocrotonic acids. In order to find out the laws governing the interesting phenomena observed in the case of isocrotonic acid, its higher homologue, angelic acid (melting point 45°), was subjected to the action of aqueous hypochlorous acid. The product of the reaction was extracted with ether, and after evaporation of the latter saturated with zinc carbonate. In this way a mixture of the zinc salts of two isomeric additive products—chlorhydroxyvaleric acids—were obtained, but as these differ in solubility, the separation of the two acids was easily effected.

(a.) *The less soluble zinc salt*, on decomposition with sulphuric acid and extraction with ether, yields a hydroxyvaleric acid crystallising in long, thin prisms, easily soluble in water, ether, and alcohol. It melts at 75° . Its formula is that of β -chloro- α -methyl- α -hydroxybutyric acid, $\text{CHClMe}\cdot\text{CMe}(\text{OH})\cdot\text{COOH}$, with which, comparison shows it to be identical. Its zinc salt, $(\text{C}_5\text{H}_8\text{ClO}_3)_2\cdot\text{Zn}$, forms fine threads consisting of prisms or plates. The calcium salt has an analogous composition. By the action of alcoholic potash on the acid, it is converted into the potassium salt of the corresponding glycidic acid, $\text{C}_5\text{H}_7\text{KO}_3 + \frac{1}{2}\text{H}_2\text{O}$; this crystallises in glistening prisms. The corresponding silver salt, $\text{C}_5\text{H}_7\text{AgO}_3$, forms thin scales. The free acid, α - β -dimethylglycidic acid, $\text{C}_5\text{H}_8\text{O}_3$, crystallises in microscopic prisms and smells like butyric acid. It is easily soluble in water, alcohol, and ether, and melts at 61 – 62° .

(b.) *The more soluble zinc salt* is so soluble in water that it can only be separated in the solid state by evaporation of its aqueous solution to the consistency of a syrup, and allowing it to stand for a long time, when it becomes converted into an amorphous solid. The acid, $C_5H_7ClO_3$, prepared like its isomeride, crystallises in quadratic prisms combined with a sphenoid, easily soluble in water, alcohol, and ether, and melting at 105° . The calcium, silver, and zinc salts have the same empirical formulæ as those of the acid (a). The potassium salt, $C_5H_5ClKO_3$, does not undergo any change, even if its alcoholic solution is boiled in the presence of a small excess of potash; in this it differs from the salt of α -chlor- α -methyl- β -hydroxybutyric acid, obtained from tiglic acid, which under these conditions is easily decomposed with separation of potassium chloride. Another difference between the two acids is in the properties of their silver salts as well as of the free acids themselves, the α -chloro- α -methyl- β -hydroxybutyric acid melting at 62° . The corresponding glycidic acid could not be obtained. The author draws the following general conclusions: (1.) When hypochlorous acid unites with those unsaturated acids which are capable of an isomeric conversion, that is, of conversion from a less stable to a more stable form, two isomeric chlorhydroxy-acids are formed. (2.) One of these chlorinated acids is a derivative of the more stable form of unsaturated acid and identical with those chlorhydroxy-acids which are obtained by the action of hydrogen chloride on the glycidic acids corresponding with the stable forms (normal crotonic and tiglic acids). (3.) The second chlorhydroxy-acid is a derivative of the less stable form of unsaturated acid. B. B.

Synthesis of Ketonic Acids. By W. WISLICENUS (*Annalen*, **246**, 306—329).—*Ethyl sodoxalacetate*, $COOEt \cdot CO \cdot CHNa \cdot COOEt$ (Abstr., 1887, 234, 587, this vol., p. 361), is prepared by the action of sodium on sodium ethoxide (free from alcohol) on an ethereal solution of ethyl oxalate and acetate. The product is purified by recrystallisation from absolute alcohol. It is insoluble in ether. *Ethyl oxalacetate*, $COOEt \cdot CO \cdot CH_2 \cdot COOEt$, obtained by decomposing the sodium-derivatives with dilute sulphuric acid, is a colourless oil boiling at 131 — 132° under 24 mm. pressure. It is miscible in all proportions with alcohol and ether. The alcoholic solution gives a dark-red coloration with ferric chloride. Ethyl oxalacetate dissolves in a dilute solution of sodium hydroxide, and this sodium salt produces precipitates in solutions of metallic salts. The barium, calcium, lead, and silver compounds are amorphous. The zinc, cobalt, nickel, magnesium, and copper compounds are deposited from alcoholic solutions in crystals. *Ethyl phenylhydrazineoxalacetate*,



crystallises in quadratic plates. It is freely soluble in alcohol and ether, and melts at 76 — 78° , but decomposes on exposure to a temperature of 100° , yielding ethyl alcohol and *ethylic phenylpyrazolone-carboxylate*, $PhN < \begin{smallmatrix} CO \\ N:C \end{smallmatrix} \begin{smallmatrix} \text{---} CH_2 \\ (COOEt) \end{smallmatrix} >$.

The pyrazolone-derivative melts at 180 — 182° and dissolves in

alcohol. It yields a yellow isonitro-compound. The free acid forms a red isonitroso-derivative. W. C. W.

Ethylic Methyloxalacetate and Ethyloxalacetate. By E. ARNOLD (*Annalen*, **246**, 329—338).—The preparation and some of the properties of ethylic methyloxalacetate have been previously described (this vol., p. 361). The phenylhydrazine-derivative crystallises in small plates, and melts at 99—100°; at 120° it decomposes, yielding the ethyl salt of 1 : 4 : 5 : 3 phenylmethylpyrazolonecarboxylic acid. The free acid is deposited from alcohol in plates, and melts at 220—221°. The ethyl salt forms needle-shaped crystals. It melts at 148—149°, and dissolves freely in ether, chloroform, and benzene.

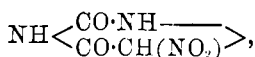
Ethylic ethyloxalacetate, $\text{COOEt} \cdot \text{CO} \cdot \text{CHEt} \cdot \text{COOEt}$, is prepared by the action of sodium ethoxide (free from alcohol) on a mixture of ethyl oxalate and butyrate. It is a liquid boiling at 136—138° under 20 mm. pressure. Ferric chloride produces a red coloration. Ethylic ethyloxalacetate is decomposed by boiling with dilute sulphuric acid, yielding butyrylformic acid. W. C. W.

Action of Ethyl Iodide and Zinc on Ethyl Malonate. By S. SCHUKOFFSKY (*J. Russ. Chem. Soc.*, 1887, 601—604).—When a mixture of ethyl malonate with ethyl iodide is heated with zinc, using a reflux condenser, large quantities of a gas are given off which is not absorbed by bromine. The principal product of the reaction is the ethyl salt of diethylmalonic acid, $\text{C}_2\text{Et}_2(\text{COOEt})_2$, a liquid boiling at 220°, and having the sp. gr. 1.0071 at 0°, and 0.9901 at 15°. The free diethylmalonic acid was obtained by hydrolysis of the ethyl salt with alcoholic potash, and the calcium, sodium, potassium, and silver salts were prepared. When heated to 170—180°, diethylmalonic acid is decomposed into carbonic anhydride and diethylacetic acid.

B. B.

Oxytetric and Hydroxytetric Acids. By A. GORBOFF (*J. Russ. Chem. Soc.*, 1887, 605—615).—Demarçay's tetric acid and its homologues of the supposed general formula $\text{C}_{3(m+3)}\text{H}_{6(m+1)} + 2\text{O}_7$, have, according to W. Pavloff's investigation, the general formula $\text{C}_n\text{H}_{2n-4}\text{O}_3$, and his oxytetric series of the formula $\text{C}_{6(m+3)}\text{H}_{3(m+1)} + 2\text{O}_{10}$, most probably (as pointed out by Beilstein) the formula $\text{C}_n\text{H}_{2n-4}\text{O}_4$, which, as the author shows, although at first sight probable, is not in accordance with Demarçay's analytical results. The author has compared at length the physical and chemical properties of oxytetric acid, its derivatives, and salts with those of *mesaconic acid*, $\text{C}_3\text{H}_4(\text{COOH})_2$, and finds a striking agreement, which leads him to believe in their identity. The *oxytetric acid* would then be identical with hydromucic acid, the *oxyhexic acid* with terebic acid, and the *hydroxytetric acid* with pyrotartaric acid, as shown in a table comparing them. The *hydroxytetric acid* is ethyltartaric acid, the *hydroxyhexic acid* propylsuccinic acid, and the *hydroxyisohectic acid* is isopropyltartaric acid. B. B.

Derivatives of Carbamide. By A. P. N. FRANCHIMONT and E. A. KLOBBIE (*Rec. Trav. Chim.*, **7**, 12—24).—*Nitrohydantoin*,



prepared by evaporating a solution of hydantoin with five times its weight of nitric acid, crystallises from alcohol in short prisms, and from water in small, shining needles melting at about 170° with decomposition (compare Franchimont, this vol., pp. 1052 and 1064).

Nitrolactylcarbamide, $\text{NH} \left\langle \begin{array}{c} \text{CO} \text{---} \text{NH} \\ \text{CO} \cdot \text{CMe}(\text{NO}_2) \end{array} \right\rangle$, prepared in like manner, crystallises from water and alcohol in rhombic plates, melts at about 148° with decomposition, and is readily soluble in water, rather less so in alcohol, and almost insoluble in ether, benzene, and chloroform. It is decomposed when boiled with water.

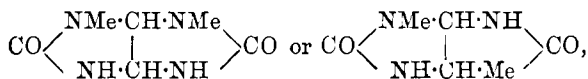
α -*Ureidopropionamide*, $\text{CONH}_2 \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CONH}_2$, was obtained in the preparation of lactylcarbamide by Heintz's method. It crystallises from alcohol in small, slender needles, melts at 196° , and is soluble in water, but insoluble in ether. When heated with hydrochloric acid, it yields lactylcarbamide and ammonium chloride.

α -*Ureidopropionitrile*, $\text{CONH}_2 \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CN}$, also obtained in the preparation of lactylcarbamide, crystallises in small prisms, melts at 106° , and is very readily soluble in water and alcohol, but only very sparingly in ether. When heated with hydrochloric acid, it yields lactylcarbamide and ammonium chloride.

Dinitroethylenecarbamide, $\text{CO} \left\langle \begin{array}{c} \text{NH} \cdot \text{CH}(\text{NO}_2) \\ \text{NH} \cdot \text{CH}(\text{NO}_2) \end{array} \right\rangle$, obtained by treating ethylenecarbamide with five times its weight of nitric acid, crystallises in colourless prisms, melts at 210° with decomposition, and is sparingly soluble in alcohol and water. When it is boiled with water, carbonic anhydride is evolved, the solution becomes strongly acid, and on evaporation a crystalline compound is obtained. This product has the composition of a dinitroethylenediamine; it melts at about 174° with decomposition, is soluble in water and alcohol, and is immediately decomposed by concentrated sulphuric acid or nitric acid with evolution of nitrous oxide (2 mols.). The potassium salt crystallises in colourless needles, melts at 210° , and is insoluble in absolute, but soluble in dilute, alcohol.

Dinitroglycolurile, $\text{CO} \left\langle \begin{array}{c} \text{NH} \cdot \text{C}(\text{NO}_2) \cdot \text{NH} \\ | \\ \text{NH} \cdot \text{C}(\text{NO}_2) \cdot \text{NH} \end{array} \right\rangle \text{CO}$, prepared by nitrating glycolurile, is almost insoluble in boiling water or alcohol, and decomposes at about 217° without melting. When boiled with water, it is decomposed into carbonic anhydride (1 mol.), nitrous oxide (2 mols.), and a colourless, crystalline compound which is insoluble in most ordinary solvents.

Glycoldimethylurile,



prepared by treating an aqueous solution of a mixture of glyoxal and methylcarbamide with hydrochloric acid, crystallises from boiling

water in slender needles, begins to melt at 210° , and fuses completely at 260° . It is readily soluble in boiling water, sparingly in alcohol, and insoluble in ether and light petroleum.

*Dinitroglycoldimethyluril*e, $C_6H_8N_6O_6$, is a white powder, insoluble in boiling water or alcohol, and is not decomposed when boiled with water.

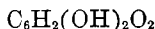
Isosuccinic-ureid, $CHMe<\begin{smallmatrix} CO\cdot NH \\ CO\cdot NH \end{smallmatrix}>CO$, obtained by heating a mixture of isosuccinic acid and carbamide with phosphorus oxychloride, sublimes at about 190° in a partial vacuum, forming long, colourless, shining plates, melts at 192° , and is readily soluble in water and alcohol, but only sparingly in ether. When treated with nitric acid, it yields a compound which crystallises in needles and is readily soluble in water, ethyl alcohol, methyl alcohol, and ether, but only sparingly in chloroform and benzene, and insoluble in light petroleum. Its composition is $C_{20}H_{22}N_{12}O_{23}$. F. S. K.

Constitution of Benzene. By A. LADENBURG (*Annalen*, **246**, 382—384).—The author maintains that Baeyer's proposed formula for benzene is identical with Claus's diagonal formula for benzene. So long as we regard the carbon-atom as having four equal affinities, Claus's formula cannot be reconciled with the existence of three isomeric benzene substitution products. W. C. W.

Configuration of the Benzene Molecule. By H. SACHSE (*Ber.*, **21**, 2530—2538).—The arrangement ascribed to the benzene molecule is shown by a model constructed as follows:—Two parallel triangles are removed from a cardboard model of an octahedron and a regular tetrahedron placed on each of the remaining six triangles, so that the latter form the bases of the tetrahedra. These represent the six carbon-atoms, whilst the hydrogen-atoms are supposed to be situated at the free angles. The ring thus formed of six carbon-atoms is more stable than a ring formed of any other number of carbon-atoms, as each atom is so attached to the two next atoms that it is in equilibrium, and as a periodic movement of single carbon-atoms is not possible, the system can only move as a whole.

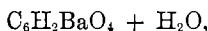
The constitution of naphthalene and pyrene based on the above benzene formula is also discussed. N. H. M.

Dihydroxyquinone and Tetrahydroxybenzene. By R. NIETZKI and F. SCHMIDT (*Ber.*, **21**, 2374—2379).—*Dihydroxyquinone*,



(symmetrical), is formed when the diamidoresorcinolimide, prepared by Typke's method, is dissolved in 10 parts of 10 per cent. potash or soda, and the solution kept at 70° until, on adding hydrochloric acid to a small portion, straw-coloured needles are precipitated. Alkali is then added, and the salt which separates from the cold solution dissolved in water, and decomposed by an acid. The quinone is readily soluble in alcohol, glacial acetic acid, and ethyl acetate, crystallising from the last-named solvent in dark-yellow, indented needles which

have a bluish tinge; it is almost insoluble in cold, and only sparingly soluble in hot water, and is decomposed when the solution is boiled. It sublimes rather readily without melting. When treated with fuming nitric acid, it yields nitranilic acid. The *sodium*-derivative, $C_6H_2(ONa)_2O_2$, and the potassium-derivative are readily soluble in water, yielding red solutions from which they crystallise in long, dark-red needles; they are sparingly soluble in alkalis and alcohol, and when precipitated by these reagents and dried are obtained in the form of an orange-yellow powder. The *barium*-derivative,



is sparingly soluble in water, and crystallises in almost black needles with a bluish reflex. The *silver*-derivative is amorphous, and when treated with methyl alcohol and methyl iodide yields the *methyl*- and *dimethyl*-derivatives. The latter crystallises in bright yellow plates, and can be separated from the former by means of ammonia, in which it is soluble. It decomposes when heated to 220° , does not give a red coloration with concentrated sulphuric acid, and when treated with bromine yields a colourless, viscous substance. The *oxime*, $C_6H_2(OH)(NOH)_2$, crystallises in colourless plates and dissolves in alkalis, forming a brown solution from which it is precipitated unchanged by acids.

Tetrahydroxybenzene, $C_6H_2(OH)_4$, [$H_2 = 1 : 4$], prepared by warming the preceding compound with stannous chloride, is very readily soluble in water, alcohol, and ether, moderately soluble in hydrochloric acid or glacial acetic acid, and crystallises from the last-named solvent in greyish plates melting at $215-220^\circ$. Aqueous solutions quickly become brown on exposure to the air, and alkaline solutions are soon converted into solutions of the corresponding salt of the dihydroxyquinone. Ferric chloride precipitates the dihydroxyquinone from aqueous solutions of the tetrahydroxy-compound. The *acetyl*-derivative, $C_6H_2(OAc)_4$, crystallises from glacial acetic acid in small, colourless, rhombic plates melting at 217° .

The dihydroxyquinone and tetrahydroxybenzene described above are not identical with the compounds described under the same names by Loewy (Abstr., 1886, 1028). F. S. K.

Dichroïns obtained by the Action of Aqua Regia and Bromine Aqua Regia. By H. BRUNNER and P. CHUIT (*Ber.*, 21, 2479—2486).—*Monochloro- α -pentaesorcinoldichroïn ether*, $C_{66}H_{48}ClN_3O_{18}$, is obtained by heating 15 grams of resorcinol, 60 grams of water, 20 c.c. of nitric acid (sp. gr. = 1.39), and 60 c.c. of hydrochloric acid (sp. gr. = 1.2) for half an hour on a water-bath. It is a dark violet substance, of metallic lustre, insoluble in chloroform, benzene, and carbon bisulphide, soluble in alcohol and ether; the alkaline solution is of a pure blue colour, with a brown fluorescence. The *acetyl*-derivative, $C_{66}H_{40}Ac_5ClN_3O_{18}$, prepared by heating the dye with 3 parts of acetic anhydride and 2 parts of dry sodium acetate at 120° for two hours, forms a red, amorphous mass, sparingly soluble in water, soluble in alcohol, chloroform, and benzene.

Monobromo- α -tetraesorcinoldichroïn ether, $C_{48}H_{35}BrN_2O_{13}$, is formed

when 15 grams of resorcinol, 70 c.c. of water, 60 c.c. of hydrobromic acid (sp. gr. = 1.49), and 20 c.c. of nitric acid (sp. gr. = 1.39), are heated in a large flask on a water-bath. The product is washed with water, dried, extracted with benzene, which removes a brown substance, and dissolved in ether. It is a brownish-violet substance of metallic lustre, readily soluble in alcohol and acetone, almost insoluble in chloroform and benzene. The *acetyl-derivative*, $C_{48}H_{29}Ac_6BrN_2O_{13}$, is an orange-red, amorphous powder, melts at 120° , and dissolves readily in hot alcohol. When the pure dye is heated at 120° , the *anhydride*, $C_{48}H_{33}BrN_2O_{12}$, is formed. This dissolves in alkalis, with violet colour and brown fluorescence. The sparingly soluble dichroïn has the formula $C_{36}H_{27}BrN_2O_{11}$.

Monochloro- α -orcinoïdichroïn, $C_{21}H_{20}ClNO_6$, was prepared by Reymann (*Ber.*, **13**, 809), who ascribed to it the formula $C_{21}H_{17}ClN_2O_6$. It is best prepared by heating 10 grams of orcinol, 10 c.c. of nitric acid, and 30 c.c. of hydrochloric acid on a water-bath, washing the product with water, dissolving in ammonia or soda, and precipitating with acid. When dried, it acquires a greenish colour and metallic lustre; it is soluble in alcohol, ether, and acetone, insoluble in benzene and chloroform. The *acetyl compound*, $C_{21}H_{16}Ac_2ClNO_6$, dissolves readily in benzene and chloroform, sparingly in alcohol.

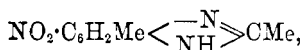
When orcinol (4 grams) dissolved in a little hot water is heated on a water-bath with nitric acid (sp. gr. = 1.39, 10 c.c.), and hydrobromic acid (sp. gr. = 1.49, 30 c.c.), a red substance of the formula $C_{48}H_{27}Me_3BrN_2O_3$ is obtained. This dissolves in alkalis, yielding a peach-coloured solution with a red fluorescence. *Monobrom- α -orcinoïdichroïn*, $C_{21}H_{20}BrNO_6$, is also formed in the reaction. It is a brown powder, soluble in alcohol and hot water, almost insoluble in ether and benzene; the solution in alkalis is reddish-violet, with a brown fluorescence.

Aqua regia acts on phenol with formation of a red dye, which dissolves in alkalis with deep blue colour. When hydrobromic acid is used, a crystalline compound resembling dibromorthonitrophenol is obtained. It melts at 115° ; the lead, barium, potassium, sodium, and silver salts are respectively yellowish-red, orange-yellow, red-yellow, and red. Dichroïns are therefore only formed when the nitrogen-atom is in the para-position. The dichroïns obtained from resorcinol and orcinol belong to the α -series, and contain the group $C_6N(O \cdot C_6)_2$.
N. H. M.

Decomposition Products of Panicole. By G. KASSNER (*Arch. Pharm.* [2], **26**, 536—541).—Panicole, obtained by the author from the fatty oil of millet as the crystallised constituent of that oil, (*Arch. Pharm.* [3], **25**, 395), was considered most probably to be a mixed ether, and not an alcohol. Under the action of hydriodic acid in a sealed tube at 150° , methyl iodide was produced. The formula of panicole being $C_{13}H_{20}O$, and methyl iodide being obtained from it, as stated above, the compound must be a mixed ether, and contain a methoxyl-group. The reaction with hydriodic acid was not perfectly satisfactory, but with fuming hydrochloric acid, and some chloroform to increase the surfaces in contact, the decomposition was complete

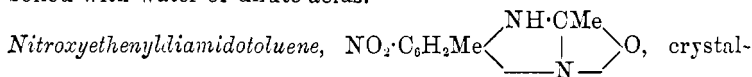
after heating at 160° in a sealed tube for several hours. Methyl chloride was obtained, and also a solid which melted at 78° (panicole melts at 285°), but could not be obtained in a crystalline form; its composition was $C_{12}H_{17}\cdot OH$. Hence panicole has the formula $C_{12}H_{17}\cdot OCH_3$. The substance, $C_{12}H_{17}\cdot OH$, is a tertiary alcohol, a phenol. Concentrated sulphuric acid turns it raspberry-red, and dissolves it; on pouring this solution into much water, a light flocculent precipitate is thrown down, probably as a sulphonic acid. A complete crystallographic description of panicole is given. J. T.

Reduction-products of Metadinitroparacetotoluide. By Z. BANKIEWICZ (*Ber.*, **21**, 2402—2411).—*Nitroethenyldiamidotoluene*,



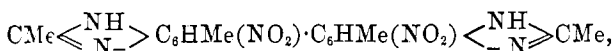
prepared by treating metadinitracetotoluide with a slight excess of alcoholic ammonium sulphide, crystallises from dilute alcohol or hot water in slender needles, melts at 246° , is very readily soluble in alcohol, sparingly in ether, and almost insoluble in cold water or soda. It yields ethenyldiamidotoluene when reduced with tin and hydrochloric acid (compare Niementowski, *Abstr.*, 1886, 544). The *hydrochloride*, $C_8H_9N_3O_2\cdot HCl$, crystallises from water in large, well-defined prisms, and is readily soluble in alcohol. The *sulphate* is very readily soluble in alcohol and alcoholic ether, and crystallises in long, colourless needles. The *nitrate* crystallises in yellow, transparent plates, and melts at 207° ; it is moderately soluble in cold, and readily in hot water.

When dinitracetotoluide is treated with alcoholic ammonium sulphide, in quantity insufficient for complete reduction, and the reduction-product mixed with soda, nitroethenyldiamidotoluene and hydrazodinitracetotoluide remain, and the solution contains three compounds, which are precipitated on adding acetic acid. (1.) An azoxy-compound, which is very sparingly soluble in hot alcohol, and melts at 236° . (2.) An azo-compound, which is readily soluble in hot alcohol, and crystallises in brown needles melting at 242 — 244° . (3.) Nitroxyethenyldiamidotoluene, which is formed when the reduction-product is boiled with water or dilute acids.



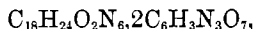
lises in shining, green needles containing water, melts at 255 — 256° , and is readily soluble in hot water or dilute alcohol, but only very sparingly in absolute alcohol, ether, or benzene. It dissolves in soda with a red coloration, and is also soluble in concentrated ammonia. It is not acted on at 200° by concentrated hydrochloric acid, and is not hydrolysed by alcoholic potash. When treated with nitrous acid, it yields crystalline, unstable nitroso-compounds. It yields diamidoacetotoluide (Niementowski, *loc. cit.*), when reduced with tin and hydrochloric acid. The hydrochloride is crystalline.

Dinitrodiethenyldiamidotolyl,



is obtained when hydrazodinitracetotoluide (see above) is treated with dilute hydrochloric acid. It crystallises in long prisms or microscopic needles, melts at 242° , is readily soluble in ethyl and methyl alcohol, moderately soluble in hot water, but only sparingly in ether and soda. The *sulphate* crystallises in concentrically grouped needles, and is readily soluble in water, but only sparingly in alcohol. The *hydrochloride*, $\text{C}_{18}\text{H}_{15}\text{N}_5\text{O}_4 \cdot 2\text{HCl}$, crystallises in colourless, flat needles, and sublimes at 100° . The *nitrate* crystallises from water in thick, yellowish needles melting at $213\text{--}214^\circ$ with decomposition.

Diacetohexamidoditolyl, $\text{NHAc} \cdot \text{C}_6\text{HMe}(\text{NH}_2)_2 \cdot \text{C}_6\text{HMe}(\text{NH}_2)_2 \cdot \text{NHAc}$, prepared by reducing the preceding compound with tin and hydrochloric acid, crystallises with 5 mols. H_2O , melts at 196° , and is very readily soluble in alcohol, moderately in ether and benzene, but almost insoluble in water. It oxidises quickly in hot alcoholic solution. The *hydrochloride*, $\text{C}_{18}\text{H}_{24}\text{O}_2\text{N}_6 \cdot 2\text{HCl} + 2\text{H}_2\text{O}$, crystallises in colourless needles, and is very readily soluble in water. The *picrate*,



and the *nitrate* crystallise in red needles.

F. S. K.

Trinitrometaphenylenedimethyldinitramine. By P. VAN ROMBURGH (*Rec. Trav. Chim.*, **7**, 1—11).—Pure tetramethylmetaphenylenediamine melts at -2° , and boils at $266\text{--}267^\circ$ (748 mm. pressure) (compare Wurster and Morley, *Ber.*, **12**, 1814). It combines with symmetrical trinitrobenzene (1 mol.), yielding a product which crystallises in long, almost black, shining needles melting at 121° ; it also combines with metadinitrobenzene (1 mol.); the product crystallises in dark, garnet-red needles, which melt at 58° .

Trinitrometaphenylenedimethyldinitramine, $\text{C}_6\text{H}(\text{NO}_2)_3(\text{NMe} \cdot \text{NO}_2)_2$, is obtained by gradually adding tetramethylmetaphenylenediamine, dissolved in twice its volume of concentrated sulphuric acid to nitric acid of sp. gr. 1.48. It can be crystallised from alcoholic acetone, but is almost insoluble in most ordinary solvents, excepting acetone, and is decomposed when heated at about 205° . It yields methylamine when boiled with dilute potash.

Trinitrodimethylmetaphenylenediamine, $\text{C}_6\text{H}(\text{NO}_2)_3(\text{NHMe})_2$, obtained by boiling the preceding compound with phenol, separates from phenol in small, yellow crystals melting at 235° with decomposition. It is sparingly soluble in acetic acid and all ordinary solvents, and less readily in acetone than the nitramine. It is reconverted into the nitramine by cold, concentrated nitric acid, and when boiled with very dilute potash it yields methylamine and trinitroresorcinol. Its constitution is probably $[(\text{NHMe})_2 : (\text{NO}_2)_3 = 1 : 3 : 2 : 4 : 6]$.

F. S. K.

Chromogenic Carbins: Constitution of Rosaniline Salts. By V. v. RICHTER (*Ber.*, **21**, 2475—2478).—Ethyl dinitrophenylacetate is formed in almost theoretical quantity by the action of orthoparadinitrobenzene on the sodium-derivative of ethyl

orthoparadinitrophenylacetate. The reaction confirms the presence of a CH-group in the compound (compare this vol., p. 1189).

Paranitrobenzyl cyanide (Gabriel, *Ber.*, **14**, 2342) dissolves in alcoholic potash or soda with intense carmine-red coloration and formation of salts, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHX} \cdot \text{CN}$. Orthonitrobenzyl cyanide, on the other hand, dissolves in alcoholic alkali with intense violet-blue coloration (Bamberger, *Abstr.*, 1887, 131).

When orthoparadinitrobenzene is added to an alcoholic solution of paranitrobenzyl cyanide and sodium ethoxide, an intensely violet-blue solution is obtained. The product, which is probably *paranitrophenyl-orthoparadinitrophenylcarbin cyanide*, $\text{CN} \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NO}_2) \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$, is almost colourless, dissolves in alkalis, ammonia, and alkaline carbonates with intense dark blue coloration, and is precipitated unchanged on addition of an acid. The *sodium*-derivative is a greenish-black amorphous powder.

The name carbin-dyes is ascribed to the above compounds, as well as to the rosaniline salts, which are probably similarly constituted, carbin being the name for all methane-derivatives in which positive or negative groups are substituted for two or three hydrogen-atoms, and the remaining atom or atoms can be readily displaced by radicles of the opposite character. The acid carbins, as for instance trinitrophenylcarbin, $\text{CH}(\text{C}_6\text{H}_4 \cdot \text{NO}_2)_3$, and the carbin bases, as triamido-phenylcarbin, are colourless, whilst the salts $\text{CNa}(\text{C}_6\text{H}_4 \cdot \text{NO}_2)_3$ and $\text{CCl}(\text{C}_6\text{H}_4 \cdot \text{NH}_2)_3$ are coloured.

N. H. M.

Eurhodines. By O. N. WITT (*Ber.*, **21**, 2418—2421).—The author proposes to extend the name of "eurhodine" to all polyamido-derivatives of azines, and that of "saffranine" to all amido-derivatives of azonium bases. The saffranines and eurhodines are closely related to the indamines, which are very often formed as intermediate products in the preparation of these dyes. To determine whether this intermediate formation of an indamine is necessary, the author endeavoured to obtain dyes from metaxylylenediamine, $[\text{Me} : (\text{NH}_2)_2 = 1 : 3 : 4 : 6]$, which he prepared by reducing metanitrometaxylydine. Metaxylylenediamine is not unstable as stated by Fittig, Ahrens, and Mattheides (*Annalen*, **147**, 18). The *hydrochloride* crystallises in white needles.

When the hydrochloride is well mixed with dry sodium acetate (1 mol.) and nitrosodimethylaniline (1 mol.), and the mixture covered with glacial acetic acid and boiled, a violent reaction takes place, but no eurhodine is formed. Metaxylylenediamine and quinonechlorimide in acetic acid solution do not yield a dye.

These results show that this diamine which cannot form an indamine is also unable to produce a eurhodine, and consequently the number of eurhodines which can be formed by this method is considerably limited.

Metaxylylenediamine does not show the usual reactions of metadamines; it does not yield vesuvin when treated with sodium nitrite, and when mixed with diazobenzenesulphonic acid and sodium acetate no chrysoidinesulphonic acid is formed. It is, however, readily diazotised, and an aqueous solution of the diazo-compound forms a

brown azo-dye with metatoluylenediamine, the properties of which coincide with those of the typical toluylene-brown; it also forms a red dye with α,α -naphtholsulphonic acid and a reddish-brown dye with Brønner's β -naphthylaminesulphonic acid. F. S. K.

Derivatives of Carbizin and Thiocarbizin. By M. FREUND and B. B. GOLDSMITH (*Ber.*, **21**, 2456—2469).—The compounds previously described (this vol., p. 686; *Ber.*, **21**, 1240) are derivatives of carbizin, $\text{CO} < \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} >$.

Formylphenylcarbizin, $\text{CO} < \begin{smallmatrix} \text{NPh} \\ \text{N(CHO)} \end{smallmatrix} >$, prepared by heating a benzene solution of carbonyl chloride with formylphenylhydrazide, crystallises in needles, melts at 73° , boils at $255\text{--}256^\circ$, is readily soluble in alcohol, ether, chloroform, benzene, and glacial acetic acid, moderately in carbon bisulphide, and sparingly in water. It is reconverted into the hydrazide when boiled with sodium carbonate.

Acetylphenylcarbizin (*loc. cit.*) is converted into acetylphenylhydrazine when boiled with sodium carbonate: and when heated with potash it is decomposed into carbonic anhydride, acetic acid, and phenylhydrazine. It is not reduced by zinc and glacial acetic acid, but when warmed with phosphorus and hydriodic acid considerable quantities of aniline hydriodide and carbonic anhydride are formed. It is completely decomposed when boiled with sodium ethoxide, or when heated with alcoholic ammonium sulphide.

Propionylphenylhydrazine, $\text{NPh}\cdot\text{NH}\cdot\text{COEt}$, prepared by heating propionamide with phenylhydrazine, crystallises from chloroform in plates, and melts at $157\text{--}158^\circ$.

Propionylphenylcarbizin, $\text{CO} < \begin{smallmatrix} \text{NH} \\ \text{N(COEt)} \end{smallmatrix} >$, obtained by heating the hydrazine with carbonyl chloride, crystallises from alcohol in white needles, and melts at $62\text{--}63^\circ$.

Benzoylphenylcarbizin, $< \begin{smallmatrix} \text{CO} \\ \text{NPh} \end{smallmatrix} > \text{N}\cdot\text{COPh}$, prepared by heating benzoylphenylhydrazide with a benzene solution of carbonyl chloride, crystallises from alcohol in white needles, and from glacial acetic acid in rhombic plates which melt at $113\text{--}114^\circ$, and are insoluble in water.

Succinylphenylhydrazine, $\text{N}_2\text{H}_2\text{Ph}\cdot\text{CO}\cdot\text{C}_2\text{H}_4\cdot\text{CO}\cdot\text{N}_2\text{H}_2\text{Ph}$, crystallises from glacial acetic acid in yellowish plates, melts at $208\text{--}209^\circ$, and is sparingly soluble in alcohol.

Succinylphenyldicarbizin, $< \begin{smallmatrix} \text{NPh} \\ \text{CO} \end{smallmatrix} > \text{N}\cdot\text{CO}\cdot\text{C}_2\text{H}_4\cdot\text{CO}\cdot\text{N} < \begin{smallmatrix} \text{NPh} \\ \text{CO} \end{smallmatrix} >$, melts at 225° .

Phenylcarbizincarboxylamide, $< \begin{smallmatrix} \text{CO} \\ \text{NPh} \end{smallmatrix} > \text{N}\cdot\text{CO}\cdot\text{NH}_2$, is obtained when finely divided phenylsemicarbazide is mixed with a benzene solution of carbonyl chloride, the mixture kept for 8 to 10 hours, and the benzene evaporated at the ordinary temperature. It crystallises from hot alcohol in needles, melts at $166\text{--}167^\circ$, is moderately soluble in benzene and chloroform, sparingly in water, and insoluble in ammonia and alkalis.

Diphenylsemicarbazide is obtained by mixing phenylhydrazine and phenyl cyanate in ethereal solution. (Compare Skinner and Rubeman, this vol., p. 552.) It melts at 173°.

Phenylcarbazinecarboxyanilide, $\langle \begin{smallmatrix} \text{NPh} \\ \text{CO-} \end{smallmatrix} \rangle \text{N} \cdot \text{CO} \cdot \text{NHPh}$, crystallises from glacial acetic acid in needles, melts at 173°, and is soluble in alcohol, but only very sparingly soluble in water.

Phenylcarbazineanthiamide, $\langle \begin{smallmatrix} \text{NPh} \\ \text{CO-} \end{smallmatrix} \rangle \text{N} \cdot \text{CS} \cdot \text{NH}_2$, the reaction product of phenylthiosemicarbazide and carbonyl chloride, separates from glacial acetic acid in microscopic crystals, melts at 270°, is sparingly soluble in glacial acetic acid, and insoluble in most solvents except aniline.

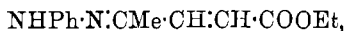
Phenylcarbazineanthianilide, $\langle \begin{smallmatrix} \text{NPh} \\ \text{CO-} \end{smallmatrix} \rangle \text{N} \cdot \text{CS} \cdot \text{NHPh}$, crystallises from hot alcohol, carbon bisulphide or benzene in needles, melts at 188°, and is very readily soluble in chloroform, but insoluble in water.

Acetylphenylthiocarbazin, $\langle \begin{smallmatrix} \text{NPh} \\ \text{CS-} \end{smallmatrix} \rangle \text{N} \cdot \text{Ac}$, prepared by heating acetylphenylhydrazine with carbon thiochloride in benzene solution, crystallises from alcohol in prisms, melts at 73–74°, and boils at 275°. It is readily soluble in ether, chloroform, benzene, carbon bisulphide, and acetone, but insoluble in water. When boiled with mercuric oxide and alcohol, it yields acetylphenylcarbazin. It is isomeric with the compound described by Fischer (*Annalen*, **202**, 126), the constitution of which is probably $\langle \begin{smallmatrix} \text{NPh} \\ \text{N} \end{smallmatrix} \rangle \text{CS} \cdot \text{Ac}$.

Benzoylphenylthiocarbazin, $\langle \begin{smallmatrix} \text{NPh} \\ \text{CS-} \end{smallmatrix} \rangle \text{N} \cdot \text{COPh}$, prepared in like manner, crystallises from alcohol in slender, white needles, melts at 110°, is readily soluble in chloroform, ether, and benzene, moderately so in alcohol and light petroleum, but insoluble in water. It yields benzoylphenylcarbazin when boiled with alcohol and mercuric oxide.

F. S. K.

Action of Phenylhydrazine on the Alkyl Salts of Halogen Ketonic Acids and Halogen Ketones. By G. BENDER (*Ber.*, **21**, 2492–2498).—*Ethyl phenylhydrazineacetylacrylate*,



is prepared by mixing solutions of ethyl bromolevulinate and phenylhydrazine in four parts of absolute alcohol, which have been previously cooled at 0°. The whole is then kept for 24 hours at the ordinary temperature. The product is filtered, the crystals dried on porous plates, powdered, washed with water, and crystallised from absolute alcohol. It forms yellow scales, melts at 117.5°, and is readily soluble in hot alcohol. When reduced with tin and hydrochloric acid, methylindoleacetic acid is formed. *Phenylhydrazineacetylacrylic acid*, $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_2$, crystallises in splendid, dark yellow crystals which melt at 157° with effervescence.

Phenylhydrazine reacts with ethyl chlorolevulinate with formation of two compounds; the one is readily soluble and melts at 123°, the other,

$C_{14}H_{21}O_4N_2$, which is sparingly soluble, melts at 205° with evolution of gas.

Bromine acts on ethyl benzoylacetate with formation of two compounds, one of which is readily soluble, and melts at $130-132^\circ$; the other crystallises in sparingly soluble, brick-red needles melting at 165° .

When dibromacetophenone (1 mol.) is kept for two days with phenylhydrazine (4 mols.), the compound $NHPh \cdot N:CPh \cdot CH:N \cdot NHPh$ is obtained. This crystallises from alcohol in intensely yellow prisms melting at 148° .

When 5 grams of chloracetone dissolved in 5 to 6 vols. of absolute alcohol is quickly added to a solution of 18 grams of phenylhydrazine dissolved in 5 to 6 vols. of alcohol cooled at -16° to -18° , the whole soon solidifies to a yellow, crystalline mass. After being kept for $\frac{1}{4}$ hour in the freezing mixture, the crystals are dried, digested with water, and crystallised from alcohol. The new compound, which has the formula $C_{24}H_{26}N_6$, forms pale yellow crystals melting at $157-158^\circ$. When boiled with acetic anhydride, the compound $C_{26}H_{26}N_6O$ crystallising in pale yellow needles is obtained; it melts at 220° . When the compound $C_{24}H_{26}N_6$ is treated with sodium nitrite and acetic acid, a compound of the formula $C_{24}H_{22}N_6$ is formed; this crystallises in very lustrous, flat, reddish-brown needles melting at 104° .

N. H. M.

New Chromogenic Groups. By V. v. RICHTER (*Ber.*, **21**, 2470 2475).—The bye-product which the author obtained in the preparation of ethyl dinitrophenylacetoacetate from orthoparadinitro-bromobenzene and ethyl sodacetoacetate has already been described by Heckmann (*Annalen*, **220**, 137), who assigned to it the composition $C_{24}H_{18}N_6O_{15}$. This substance is ethyl bi-dinitrophenylacetate, and has the constitution $CH[C_6H_3(NO_2)_2]_2 \cdot COOEt$. It is best prepared by treating the sodium-derivative of ethyl dinitrophenylacetoacetate with dinitro-bromobenzene, acetic acid being also formed. The yield is two-thirds of the theoretical quantity. It is also obtained in small quantities when ethyl sodiomalonate (1 mol.) is treated with dinitro-bromobenzene, but the principal product is ethyl dinitrophenylmalonate.

Ethyl dinitrophenylmalonate, $C_6H_3(NO_2)_2 \cdot CH(COOEt)_2$, is very readily soluble in warm alcohol or ether, and crystallises in thick, yellowish prisms, melting at 51° . It dissolves in alkalis with a red coloration and is precipitated unchanged by acids. The *sodium-derivative*, obtained by mixing the ethyl salt with concentrated soda, is insoluble in moderately concentrated alkalis, but dissolves in water with a brown coloration forming a solution from which acids precipitate the pure ethyl salt.

Ethyl bi-dinitrophenylacetate is obtained when this sodium compound is treated with dinitro-bromobenzene in alcoholic solution. It is sparingly soluble in alcohol and ether, and yields a *sodium-derivative*, $C_{18}H_{11}NaN_4O_{10}$, which crystallises in golden plates and explodes when heated at about 80° , or when heated with concentrated sulphuric acid. This sodium salt is very hygroscopic and absorbs carbonic anhydride from the air. The sodium and potassium salts dissolve in

water or alcohol, forming deep-blue solutions which are decolorised on exposure to the air, but regain their colour when alkalis are added.

These experiments show that the chromogenic nature of these compounds is due to the substitution of metals for the hydrogen of the CH_2 or CH group, and also to the dinitrophenyl-group with which the carbon is combined. When the compound contains one dinitrophenyl-group, it forms brownish-red salts, whereas when two such groups are present the salts are blue.

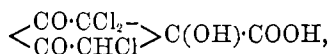
Bi-dinitrophenylmethane, $\text{CH}_2[\text{C}_6\text{H}_3(\text{NO}_2)_2]_2$, gives deep blue solutions with alcoholic potash or soda.

These chromogenic compounds may be classed with the nitro-dyes.

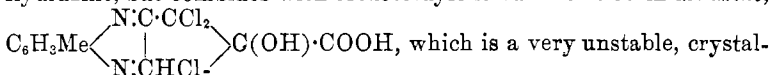
F. S. K.

Decomposition Products of Chloranilic and Bromanilic Acids. By A. HANTZSCH (*Ber.*, 21, 2421—2444).—The first product of the action of chlorine on an aqueous solution of potassium chloranilate is an additive compound, $\text{C}_6(\text{OH})_2\text{Cl}_2\text{O}_2\text{Cl}_2$, which cannot, however, be isolated as it is almost immediately converted into trichlorotriketopentamethylene (see below).

Trichlorodiketopentamethylenehydroxycarboxylic acid,



the second product of the action of chlorine on potassium chloranilate, is obtained when a solution of pure sodium hypochlorite (1 mol.) is gradually added to a solution of pure potassium chloranilate (1 mol.), the mixture acidified with hydrochloric acid and the product extracted with ether. The yield is almost theoretical. It crystallises from water in anhydrous prisms and from ether in transparent prisms which seem to contain ether. It melts at 171° with decomposition, and is very readily soluble in ether, alcohol, and water, but almost insoluble in benzene. It has a strongly acid reaction, and forms salts, most of which are amorphous and readily soluble in water, but the *lead* salt, $\text{C}_6\text{HPbCl}_3\text{O}_4$, the *mercurous* and the unstable *silver* salt, can be obtained by direct precipitation. It instantly reduces warm ammoniacal solutions of silver nitrate, and is also decomposed by a warm acid solution of silver nitrate and by concentrated alkalis. It yields sodium oxalate when treated with sodium, and when acted on by phosphorus pentachloride, an amorphous chloride is obtained. It does not react with hydroxylamine or phenylhydrazine, but combines with orthotoluylenediamine to form an *azine*,



line compound, soluble in alcohol, ether, water, and ammonia. This azine yields another very sparingly soluble yellow azine when warmed with water. The *acetyl*-derivative is amorphous and insoluble in water, but it dissolves in soda and is at the same time reconverted into the acid.

Trichlorotriketopentamethylene, $\begin{array}{c} \text{CO}\cdot\text{CCl}_2\sim \\ \text{CO}\cdot\text{CHCl} \end{array} \text{CO}$, the third product of the action of chlorine on potassium chloranilate, is prepared

by treating a neutral solution of the preceding compound with chlorine or bromine, or by acting on potassium chloranilate with a solution of sodium hypochlorite containing free chlorine. The product is precipitated with hydrochloric acid, extracted with ether, and purified by means of the ammonium-derivative. It is a colourless, crystalline, very deliquescent substance with a strongly acid reaction, and melts at 125° . It is very stable towards hot, concentrated sulphuric acid, but is very readily oxidised to oxalic acid when treated with alkaline potassium ferricyanide or other oxidising agents. The *ammonium-derivative*, $C_5(NH_4)Cl_3O_3$, is prepared by treating the acid with alcoholic ammonia and evaporating the filtered solution at the ordinary temperature. It crystallises from alcohol in yellowish prisms, melts at 207° with decomposition, is very readily soluble, and is decomposed by silver nitrate. By concentrated alkalis, both the ammonium-derivative and the substance itself are decomposed into oxalic acid and a chloride. All the metallic derivatives are readily soluble. The *monoxime*, $C_5HCl_3O_2(NOH)$, obtained by mixing the ammonium salt with hydroxylamine hydrochloride, crystallises in striated plates melting at $123-125^{\circ}$. When the ammonium-derivative is treated with an excess of hydroxylamine in alkaline solution, an oily oxime is obtained. The *azine* crystallises in yellow needles. The *hydrazide*, $C_5HCl_3(N_2HPh)_3$, is crystalline.

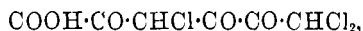
Trichlorotribromacetone, $CBBr_2Cl \cdot CO \cdot CBrCl_2$, the final product of the action of the two halogens on potassium chloranilate, is obtained when trichlorotriketopentamethylene or the hydroxy-acid is treated with an excess of bromine. It separates from ether, in which it is readily soluble, in lance-shaped crystals melting at 57° , and is insoluble in water, but slightly soluble in alcohol with decomposition. The filtrate from this product contains large quantities of oxalic acid.

Symmetrical tetrachloracetone is formed when trichlorotriketopentamethylene or the corresponding hydroxy-acid is treated with hydrochloric acid and potassium chlorate (compare Levy and Jedlicka, this vol., p. 443).

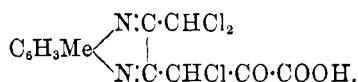
Bromanilic acid bromide, $OH \cdot C < \begin{smallmatrix} CO \cdot CBr_2 \\ CBr_2 \cdot CO \end{smallmatrix} > C \cdot OH$, is prepared by adding the calculated quantity of bromine-water to a neutral, aqueous solution of potassium bromanilate, acidifying with hydrobromic acid, extracting with ether, and, after drying over anhydrous copper sulphate, evaporating the ether in a partial vacuum as quickly as possible. As a portion of the product loses bromine very readily, and is thereby converted into the original acid, the residue is treated with chloroform in which the latter is insoluble. On evaporating the chloroform, the new acid separates in colourless prisms which melt at $184-186^{\circ}$, and soon turn red owing to loss of bromine. The acid is very readily soluble in water, yielding a strongly acid solution which probably contains a hydrate. When treated with concentrated alkalis in aqueous solution, it is readily decomposed, yielding a product which consists principally of tribromotriketopentamethylene (see below). When treated with bromine and water, it gives perbromacetone, and when heated with concentrated sulphuric acid, it is reconverted into bromanilic acid.

Tribromotriketopentamethylene, $\langle \text{CO} \cdot \text{CBr}_2 - \text{CO} \cdot \text{CHBr} \rangle \text{CO}$, is prepared by adding a solution of potassium bromate containing free bromine to an aqueous solution of potassium bromanilate until the latter becomes colourless, destroying the excess of bromine with sodium hydrogen sulphite, and proceeding as described in the case of the corresponding chlorinated derivative. It crystallises in plates, melts at 191° with decomposition, and is more sparingly soluble in water than the corresponding chloro-ketone, which it resembles both in properties and reactions. The ammonium salt, $\text{C}_5(\text{NH}_4)\text{Br}_3\text{O}_3$, crystallises in needles or plates, melts at $183-184^\circ$, and is entirely converted into *hexabromacetone*, $\text{CBr}_2 \cdot \text{CO} \cdot \text{CBr}_3$, melting at 110° , when treated with bromine and water.

Trichlorotriketovaleric or *trichlorodiacetylgluoxalic acid*,



is formed by intramolecular change when trichlorodiketopentamethylenehydroxycarboxylic acid is warmed with several times its volume of concentrated sulphuric acid. It is a crystalline compound, melts at $112-114^\circ$, and is readily soluble in all ordinary solvents, but is not deliquescent. It yields an oily chloride with phosphorus pentachloride, and shows all the properties of a ketone acid forming a crystalline *oxime* and an oily *hydrazide*. The *azine*,



crystallises in white needles and is very stable; it is readily soluble in alcohol and moderately so in ether, but almost insoluble in water. Chlorine has no action on cold, aqueous solutions of the acid, but on heating, total decomposition takes place. It is decomposed by hypochlorous acid and by a mixture of potassium chlorate and hydrochloric acid, even in very dilute solutions. When boiled with bromine and water, small quantities of trichlorotribromacetone are obtained. The *lead*, *mercurous*, and *silver* salts are sparingly soluble.

By reducing and oxidising trichlorodiketopentamethylenehydroxycarboxylic acid and trichlorodiacetylgluoxalic acid, the author has obtained a series of acids, a description of which will follow at some later date.

F. S. K.

Conversion of Hydrindonaphthene- and Indonaphthene-derivatives into Substituted Acetophenonecarboxylic Acids. By T. ZINCKE and C. GERLAND (*Ber.*, 21, 2396-2402).—*Dichloroacetophenoneorthocarboxylic acid*, $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CHCl}_2$, is obtained when dichlorodiketohydrindonaphthene is dissolved in alcohol, and concentrated potash, containing a little alcohol, is gradually added until an addition of water causes no turbidity. The solution is then acidified with hydrochloric acid, diluted with water, and the product recrystallised from hot benzene. It forms colourless, shining, monoclinic prisms, melts at 124° , is readily soluble in alcohol and glacial acetic acid, moderately soluble in benzene, and sparingly in light petroleum. It is

decomposed by soda but dissolves in sodium carbonate unchanged. The *methyl* salt, $C_{10}H_6Cl_2O_3$, forms well-defined, monoclinic crystals, and is readily soluble in alcohol and acetic acid, and moderately soluble in ether.

Trichloroacetophenoneorthocarboxylic acid, already prepared by Gabriel and Michael, is obtained in small quantities when a sodium carbonate solution of chlorhydroxynaphthaquinone is treated with chlorine, but it is best prepared by passing chlorine through a sodium carbonate solution of dichlorodiketohydrindonaphthene or dichloroacetophenonecarboxylic acid. It crystallises from acetic acid or dilute nitric acid in thick, shining needles melting at 142° . It is decomposed into phthalic acid and chloroform when treated with soda, but it dissolves in sodium carbonate unchanged.

Dichlorobromoacetophenonecarboxylic acid, $COOH \cdot C_6H_4 \cdot CO \cdot CCl_2Br$, prepared by treating the dichlorinated derivative with hypobromous acid, is very similar to the preceding compound. It melts at 150° , is not decomposed by sodium carbonate, and yields dichlorobromomethane when treated with soda.

Chlorodibromoacetophenonecarboxylic acid, $COOH \cdot C_6H_4 \cdot CO \cdot CClBr_2$, is formed when dibromodiketohydrindonaphthene is treated with hypochlorous acid or when the corresponding chlorobromo-derivative is treated with hypobromous acid. It melts at 153° , and is similar to the acids described above. Tribromoacetophenonecarboxylic acid, already prepared by Gabriel and Michael, crystallises with 1 mol. H_2O and melts at 152 — 160° .

The trihalogen-acetophenonecarboxylic acids can also be obtained by treating a sodium carbonate solution of the halogen-derivative of ketohydroxyindonaphthene with halogens. The dihalogen acids are decomposed by alkaline hypobromites or hypochlorites with formation of a salt of phthalic acid and trihalogen-derivatives of methane.

F. S. K.

Action of Ethyl Isobutyrate and of other Ethereal Salts on Ethyl Oxylate. By W. WISLIGENUS (*Annalen*, **246**, 339—341).—Attempts to effect the combination of ethyl oxalate and ethyl isobutyrate by means of sodium or sodium ethoxide were unsuccessful.

The preparation of ethyl phenyloxalacetate has been previously described by the author (*Abstr.*, 1887, 587). The phenylhydrazine-derivative crystallises in needles, melts at 69 — 70° , and dissolves freely in ether and benzene. The solution of the compound in sulphuric acid gives an intense violet-red coloration with ferric chloride.

W. C. W.

Action of Ethyl Acetate on Ethyl Phthalate. By W. WISLIGENUS (*Annalen*, **246**, 347—355).—The action of sodium on a mixture of ethyl acetate and phthalate has been previously described by the author (*Abstr.*, 1887, 587). The product is the sodium-derivative of *ethyl diketohydrindonaphthenecarboxylate* (abbreviated to *diketohydrindenecarboxylate*), $C_{12}H_8O_4Na$. It is deposited from water in yellow needles containing 1 mol. H_2O , and from hot alcohol in anhydrous crystals. The aqueous solution forms yellow precipitates with barium, calcium, and several other metallic salts. The silver

salt is crystalline and the copper compound, $(C_{12}H_9O_4)_2Cu$, is deposited from a hot alcoholic solution in green crystals.

Ethyl diketohydrindenecarboxylate, $C_{12}H_{10}O_4$, is soluble in alcohol, ether, benzene, and light petroleum, and melts with decomposition at $75-78^\circ$. Ferric chloride produces a deep-red coloration in the alcoholic solution. It is decomposed by alkalis, forming alcohol, an alkaline carbonate, and α -diketohydrindene, $C_6H_4 < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > CH_2$. The latter is best prepared by acidifying an aqueous solution of the yellow sodium compound, $C_{12}H_9O_4Na$, and extracting the mixture with ether. The residue obtained by evaporating the extract is recrystallised from light petroleum. The pure compound forms colourless needles and melts with decomposition at $129-131^\circ$. The phenylhydrazine and isonitroso-derivatives have already been described (*loc. cit.*). The dibromo-derivative, $C_6H_4(CO)_2CBr_2$, is identical with the product which Zincke and Gerland (this vol., p. 290) obtained by the action of bromine on bromamido- α -naphthaquinonimide.

The ethyl salt of methylketohydrindenecarboxylic acid is obtained by heating in sealed tubes at 120° , a mixture of methyl iodide, alcohol, and the sodium compound of ethyl diketohydrindenecarboxylate. The compound crystallises in prisms, melts at $72-74^\circ$, and dissolves freely in alcohol and ether.

W. C. W.

Action of Ethyl Oxalate on Lactones. By W. WISLICENUS (*Annalen*, **246**, 342—347).—The preparation of the sodium compound of ethyl hydrophthalylloxalate by the action of sodium ethoxide on an ethereal solution of ethyl oxalate and phthalide, has been previously described by the author (*Abstr.*, 1887, 952). The sodium compound is freely soluble in water, and the solution produces precipitates in solutions of calcium, barium, lead, copper, and silver salts. Ethyl hydrophthalylloxalate has been previously described (*loc. cit.*). The phenylhydrazine-derivative crystallises in prisms and melts at $157-159^\circ$; it dissolves freely in benzene and in hot alcohol. Ethyl hydrophthalylloxalate is decomposed by an excess of hot, dilute alkali, yielding alcohol, oxalic acid, and hydroxymethylbenzoic acid. On oxidation with nitric acid, ethyl hydrophthalylloxalate splits up into oxalic and phthalic acids.

W. C. W.

Action of Potassium Hypobromite on Amides. By S. HOOGEWERFF and W. A. VAN DORP (*Rec. Trav. Chim.*, **6**, 373—388).—*Phenylsulphondibromamide*, $SO_2Ph \cdot NBr_2$, is best prepared by dissolving 7 grams of phenylsulphonamide in an alkaline solution of potassium hypobromite containing 21 grams of bromine and 35 grams of potash in 100 c.c. of water, and adding dilute acetic acid as long as the solution remains alkaline. The product is washed with cold water, then with water at about 75° to remove the amide present, and the residue crystallised from pure chloroform. In one experiment, 8.4 grams of the dibromamide were obtained. It separates from chloroform, in which it is readily soluble, in red crystals which melt at $115-116^\circ$ or at 100° if heated for some time, and explode slightly at higher temperatures. It is unstable and is partially or entirely converted into phenylsulphon-

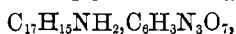
amide when treated with alcohol, ether, benzene, carbon bisulphide, or hot water. It is insoluble in cold water, but soluble in hot acetic acid and crystallises therefrom in small plates.

The *potassium* salt, $\text{SO}_2\text{Ph}\cdot\text{N}\cdot\text{KBr}$, of the bromamide is precipitated when the dibromamide is dissolved in potash, in which it is very readily soluble, and the solution mixed with concentrated potash; or when a solution of phenylsulphonamide in potassium hypobromite is treated with concentrated potash. It crystallises in small tables and decomposes with slight explosion when heated above 100° , but it is very stable in alkaline solution. It is converted into phenylsulphonamide by ammonia, and when an aqueous solution is treated with dilute acetic acid, a yellow precipitate, consisting of phenylsulphonamide and the corresponding dibromo-derivative, is obtained. The *sodium* salt, $\text{SO}_2\text{Ph}\cdot\text{N}\cdot\text{NaBr}$, prepared in like manner, is more sparingly soluble in water than the potassium salt and crystallises in small tables or leaves. The *silver* salt, $\text{SO}_2\text{Ph}\cdot\text{N}\cdot\text{AgBr} + \text{H}_2\text{O}$, crystallises in yellow prisms and is decomposed by warm water.

A compound having the composition $2(\text{SO}_2\text{Ph}\cdot\text{NBr}_2) + \text{KBr}$, is obtained when the potassium salt is treated with a solution of bromine in potassium bromide. It is decomposed by water.

Phenylacetobromamide, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{N}\cdot\text{HBr}$, is prepared by dissolving bromine (1 mol.) in an aqueous solution of potash (4 mols. KHO), and adding phenylacetamide to the solution kept at about 20° . The solution is then neutralised with acetic acid and the product crystallised from benzene, glacial acetic acid, or pure chloroform. It can also be crystallised from pure ether, in which, however, it is only sparingly soluble. It forms colourless needles, melts and turns red at $123\text{--}125^\circ$, and soon decomposes, especially in the light, even at the ordinary temperature. Cold alcohol decomposes it only very slowly, but when heat is applied, it is partially converted into the amide and the alcohol is oxidised to aldehyde. It is decomposed by ammonia, sulphurous acid, and sodium thiosulphate, with formation of the amide. It has acid properties and is readily soluble in alkalis, but when the solution is heated it is decomposed with formation of benzylamine, potassium carbonate, and potassium bromide.

Heptylamine is best prepared by dissolving caprylamide (1 mol.) in alkaline potassium hypobromite (1 mol. bromine and 4 mols. KHO in 16 times its weight of water) and distilling as quickly as possible with superheated steam. The yield is 60 to 65 per cent. Heptylamine boils at $155\text{--}156^\circ$ with the stem of the thermometer entirely in the vapour; it attracts carbonic anhydride from the air and forms with it a solid salt. The *platinochloride* decomposes between 220° and 230° and has no well-defined melting point. The *picrate*,



crystallises from dilute alcohol in needles melting at $120\text{--}121.5^\circ$.

Octylamine is best prepared by treating pelargonamide with a solution of hypobromite similar to that described above. The compound, $\text{NH}(\text{C}_8\text{H}_{17})\cdot\text{CO}\cdot\text{NH}(\text{C}_8\text{H}_{17}\text{O})$, (compare Hofmann, *Ber.*, 15, 760), soon separates from the solution. Acetic acid is then added as long as a precipitate is produced, and the bromamide obtained, after

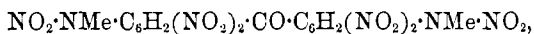
drying between blotting-paper, is mixed with lime and distilled. The yield is about 45 per cent. of the quantity which should be obtained from the bromamide employed. Octylamine boils at 179–180°, the thermometer entirely in the vapour; it attracts carbonic anhydride from the air and solidifies. The *platinochloride* decomposes above 200°, but has no definite melting point. The *picrate*, $C_8H_{17}NH_2 \cdot C_6H_3N_3O_7$, crystallises from alcohol in oblong tables and melts at 112–114°.

Phenylethylamine oxalate, $(C_8H_{11}N)_2 \cdot C_2H_2O_4$, crystallises from water in small tables and melts at 218°. The *acid salt*, $C_8H_{11}N \cdot C_2H_2O_4$, crystallises from water in needles, melts at 181°, and is decomposed by alcohol into oxalic acid and the neutral salt (compare Abstr., 1887, 245).
F. S. K.

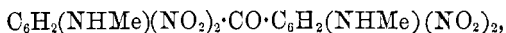
Nitramine derived from Tetramethyldiamidobenzophenone.

By P. VAN ROMBURGH (*Rec. Trav. Chim.*, 6, 365–372; compare this vol., p. 1079).—Tetramethyldiamidobenzophenone combines with symmetrical trinitrobenzene (2 mols.), yielding a compound which crystallises in long, reddish-violet needles melting at about 100°, and with 1 mol. forming a compound which crystallises in small, deep-violet plates and melts at 123°. It also combines with metadinitrobenzene (2 mols.); the product crystallises in small plates or in compact, red crystals. These additive products are stable in the air but are at once decomposed by acids.

Tetranitrodimethyldinitramidobenzophenone,



is formed when tetramethyldiamidobenzophenone is gradually mixed in the cold with nitric acid of sp. gr. 1.48 and the mixture boiled; if nitric acid of sp. gr. 1.53 is employed, the tetramethyldiamidobenzophenone takes fire. The crude product turns deep-red when poured into ammonia, but it loses this property when boiled with alcohol, and the alcoholic extract contains trinitrophenylmethylnitramine melting at 127°. Tetranitrodimethylnitramidobenzophenone forms pale-yellow crystals and is insoluble in most ordinary solvents, but sparingly soluble in acetone and acetic acid. It dissolves readily in nitric acid of sp. gr. 1.53 and when treated with hot, concentrated sulphuric acid it dissolves with evolution of gas, forming a dark-brown solution. When heated in a capillary tube above 200° for some time, it begins to decompose, at about 210–215° as a rule, but the temperature of decomposition depends greatly on the manner of heating, as it is not decomposed when heated for 30 seconds at 220°. When it is boiled with dilute potash, methylamine is evolved and a dark-brown solution obtained from which sulphuric acid precipitates a yellow product soluble in boiling water and in ammonia. It is not decomposed by boiling potassium carbonate. From this last-mentioned fact (compare van Romburgh, *Rec. Trav. Chim.*, 3, 392), and from the results obtained by Klobbie (this vol., p. 466), based on the conclusions drawn from Baither's investigations (*Ber.*, 20, 1737, Abstr., 1887, 816), the constitution of this compound is probably $[(NMeNO_2) : (NO_2)_2 : CO = 1 : 2 : 6 : 4]$ (for both rings).

Tetranitrodimethyldiamidobenzophenone,

is obtained when the preceding compound is boiled with phenol. It separates from phenol in shining, golden crystals, melts at about 225° with decomposition, and is sparingly soluble in the ordinary solvents. It dissolves in sulphuric acid, yielding a slightly coloured solution from which it is precipitated unchanged by water. When heated with nitric acid, it is reconverted into the nitramine, and when boiled with dilute potash it yields a brown solution from which acids precipitate brown flocks soluble in ammonia. F. S. K.

Action of Nitrous Acid on Tetramethyldiamidobenzophenone. By E. BISCHOFF (*Ber.*, **21**, 2452—2455).—The compound $\text{C}_{11}\text{H}_{19}\text{N}_3\text{O}_2$ is obtained when tetramethyldiamidobenzophenone is diazotised in the cold, and the product precipitated with very dilute soda. It crystallises from hot alcohol in golden-yellow plates, melts at 158 — 159° , is readily soluble in hot alcohol, benzene, and chloroform, and soluble in ether. It has basic properties and dissolves in dilute hydrochloric acid, but is reprecipitated by water. It gives Liebermann's reaction, and is reconverted into tetramethyldiamidobenzophenone when reduced with stannous chloride and hydrochloric acid. Its constitution is probably $\text{NMe}_2 \cdot \text{C}_6\text{H}_3 < \overset{\text{CO}}{\text{N}(\text{OH})} > \text{C}_6\text{H}_3 \cdot \text{NMe}_2$.

F. S. K.

Desoxybenzoïn and Desaurins. By E. NEY (*Ber.*, **21**, 2445—2452).—*Desoxybenzoïnhydrazide*, $\text{CH}_2\text{Ph} \cdot \text{CPh} \cdot \text{N} \cdot \text{NHPh}$, crystallises in slender needles, melts at 106° , and is unstable.

When methyl-desoxybenzoïn is treated with sodium ethoxide and amyl nitrite in the cold, benzoic acid and acetophenoneoxime are obtained. Desoxybenzoïn yields an orthonitro- and a paranitro-derivative when nitrated in the cold.

Paramitrodesoxybenzoïnnoxime crystallises from alcohol in needles, and melts at 107° .

Paramidodesoxybenzoïnnoxime crystallises from alcohol and melts at 141° .

Diazodesoxybenzoïn chloride gives brown dyes with alkaline solutions of α -naphthol and α -naphtholsulphonic acid.

Hydroxydesoxybenzoïn, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{COPh}$, prepared by diazotising the amido-derivative, crystallises from water in scales, melts at 129° , and is soluble in soda. The sodium salt crystallises from water in slender needles. The acetyl-derivative crystallises in plates and melts at 87° . When acetylhydroxybenzoïn is treated with carbon thiochloride and sodium ethoxide, a violent reaction takes place, and a yellow thiocarbonyl-derivative is obtained. It does not melt below 300° , dissolves in sulphuric acid with a carmine-red coloration, and is decomposed when boiled with alkalis. The chloroform solution has a green fluorescence.

Methoxydesoxybenzoïn, $\text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{COPh}$, prepared by treating the chloride of phenylacetic acid with anisöl and aluminium chloride in carbon bisulphide solution, crystallises from alcohol, melts at 76° ,

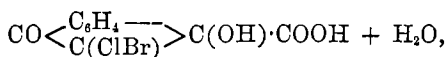
and boils at 360°. The *oxime* melts at 111°. The *benzyl*-derivative melts at 99–100°. The *methyl*-derivative, $\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{COPh}$, is an oil and boils at 330°. The *ethyl*-derivative crystallises in long prisms melting at 47°.

Phenylanisyl-desaurin, $\text{C}_{18}\text{H}_{12}\text{O}_2\text{S}$, the thiocarbonyl-derivative of methoxydesoxybenzoïn, is prepared as described above from carbon thiochloride and the benzoïn. It is a yellow substance, dissolves in chloroform with a green fluorescence, and in concentrated sulphuric acid with a blue coloration.

F. S. K.

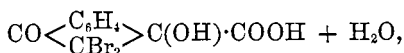
Action of Hypochlorous and Hypobromous Acids on Chlor- and Brom-hydroxynaphthaquinone and their Conversion into Hydrindonaphthene- and Indonaphthene-derivatives. By T. ZINCKE and C. GERLAND (*Ber.*, **21**, 2379–2395).—Dichloroketohydroxyhydrindonaphthenecarboxylic acid (this vol., p. 489) is prepared by passing chlorine through a 10 per cent. sodium carbonate solution of chlorhydroxynaphthaquinone until the solution commences to become turbid. A small quantity of hydrochloric acid is then added, the filtered solution mixed with an excess of hydrochloric acid, and the product, which separates after some time, recrystallised from hot, dilute sulphuric acid. It is also obtained when dichlorotriketohydronaphthalene is boiled with dilute hydrochloric acid. It crystallises from water in prisms melting at 127–128°, and from a mixture of light petroleum and ether in monoclinic prisms which melt generally at 131–132°, but at a higher temperature when heated quickly. The anhydrous acid, which can be obtained by heating carefully, crystallises from a mixture of ether and light petroleum, and melts first at 70°, and then at 135–136°. It yields chloroketohydroxyindonaphthene when heated with alkalis or baryta, and is decomposed by water at 180°.

Bromochloroketohydroxyhydrindonaphthenecarboxylic acid,

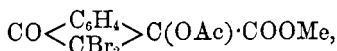


is prepared from bromohydroxynaphthaquinone as described above, or from chlorhydroxynaphthaquinone in a similar manner, employing bromine instead of chlorine; it is also obtained when chlorobromotriketohydronaphthalene is dissolved in sodium carbonate. It crystallises from hot hydrochloric acid in thick, colourless needles melting at 126–127° with decomposition, and from a mixture of ether and light petroleum in monoclinic prisms which melt at a slightly higher temperature. When heated, first at 100–115° and finally at 130°, the crystals lose 1 mol. H_2O , become opaque, and melt at 176–177°, but after recrystallising from a mixture of ether and light petroleum at 190°. The anhydrous acid takes up 1 mol. H_2O when crystallised from dilute hydrochloric acid. When boiled with water or treated with cold, dilute soda, it yields chloroketohydroxyhydrindonaphthene (compare Zincke, *Abstr.*, 1887, 728). The *methyl* salt forms monoclinic crystals melting at 134–135°. The *acetyl*-derivative of the methyl salt crystallises in small, rhombic plates melting at 136–137°.

Dibromoketohydroxyhydrindonaphthenecarboxylic acid,



prepared by treating a sodium carbonate solution of bromhydroxynaphthaquinone with bromine, or by dissolving dibromotriketohydronaphthalene in cold, dilute sodium carbonate, crystallises from hot hydrochloric acid in needles melting at 126—127°. It separates from a mixture of ether and light petroleum in large monoclinic crystals, which melt and give off water at 137—138°. The anhydrous acid melts at 170°, and crystallises unchanged from hot dilute hydrochloric acid, but after crystallising from a hot mixture of benzene and light petroleum, it melts at 165°, and seems to contain one of the solvents. When boiled with water, it is quickly decomposed, yielding bromoketohydroxyindonaphthene, which is also formed when the acid is dissolved in cold soda or baryta. The *methyl* salt crystallises in transparent prisms melting at 137°. The *acetyl*-derivative,



forms shining plates.

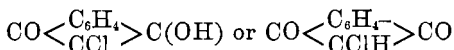
The three acids described above are very similar in appearance and behaviour, but the dichloro-compound is the most stable, and is not decomposed by cold soda.

Dichloro- α -diketohydrindonaphthene (this vol., p. 489), dissolves readily in dilute soda, and is decomposed into phthalic acid, formaldehyde, and hydrochloric acid. When treated with alcoholic potash, it is converted into dichloroacetophenonecarboxylic acid (compare this vol., p. 1193).

Chlorobromo- α -diketohydrindonaphthene (this vol., p. 290) is formed by the action of chlorine on bromoketohydroxyindonaphthene, or by the action of bromine on the corresponding chlorinated derivative. It crystallises from glacial acetic acid or alcohol in colourless plates, melts at 146—147°, and yields dibromochloromethane, chloroketohydroxyindonaphthene and phthalic acid when treated with dilute soda. Alcoholic potash decomposes it into chlorobromoform, chloroketohydroxyindonaphthene and other compounds, amongst which is probably dibromacetophenonecarboxylic acid (*loc. cit.*).

Dibromo- α -diketohydrindonaphthene (this vol., p. 290) yields bromoform, phthalic acid, and bromoketohydroxyindonaphthene when treated with alkalis. It is decomposed by alcoholic potash in a manner similar to the preceding compound.

Chloroketohydroxyindonaphthene,



(Zincke, *loc. cit.*), can be obtained by dissolving chlorobromoketohydroxyhydrindonaphthenecarboxylic acid in dilute alkali, and after some time precipitating the product with hydrochloric acid. It yields a trihalogen-derivative of acetophenonecarboxylic acid when treated with halogens in sodium carbonate solution, but in soda solu-

tions, under the same conditions, it is decomposed into phthalic acid and a trihalogen-derivative of methane.

Bromoketohydroxyindonaphthene, already obtained by Roser and Haselhoff, is prepared in like manner from dibromodiketohydrindonaphthene or from the corresponding dibromohydroxy-acid. It is unstable, crystallises in needles, and melts at 118°. It behaves towards alkalis and halogens like the corresponding chlorinated derivative, and in acetic acid solution is easily converted into the dihalogen diketone.

F. S. K.

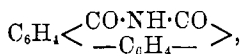
α -Naphthylamine- δ -monosulphonic Acid. By R. HIRSCH (*Ber.*, **21**, 2370—2373).— *α -Naphthylamine- δ -monosulphonic acid* is obtained when *α -naphthylamine* is heated at 125—130° for eight to nine hours with 5 parts of concentrated, but not fuming, sulphuric acid. The acid formed in the reaction is converted into the calcium salt, the latter decomposed with hydrochloric acid, and the pure compound obtained in rhombic plates by extracting repeatedly with small quantities of water and recrystallising several times from boiling water. When hydrochloric acid is added to a 1 per cent. boiling solution of the sodium salt, the acid separates in long needles, which gradually dissolve as the solution becomes cold, and change more or less completely into the rhombic plates. The acid dissolves in about 150 parts of boiling, or 450 parts of cold water, but is more sparingly soluble in alcohol and insoluble in ether and benzene. The *sodium* and *ammonium* salts are very readily soluble in water; the sodium salt separates when a solution of either salt is saturated with sodium chloride. The *potassium* and *magnesium* salts are crystalline and sparingly soluble in cold water. The diazo-derivative yields a dinitronaphthol-sulphonic acid when boiled with dilute nitric acid; the *potassium* salt of this sulphonic acid is readily soluble in water, but the *barium* salt is only sparingly soluble.

F. S. K.

An Isomeride of Oximidonaphthol. By S. MEERSON (*Ber.*, **21**, 2516—2518; compare this vol., p. 713).—Acetamidonaphthaquinone is heated with 20 parts of strong sulphuric acid on a water-bath for one hour, the *amidonaphthaquinone* precipitated with water and crystallised from alcohol, from which it separates in lustrous, brown plates, melting at 200°. The *sulphate* forms reddish needles. When oximidonaphthol (Graebe and Ludwig, *Annalen*, **154**, 318) and amidonaphthaquinone are heated with acetic anhydride, they both yield the same *triacetylamidonaphthaquinol*, $C_{10}H_5(OAc)_2NHAc$. This, by treatment with cold sulphuric acid, is converted into acetamidonaphthaquinone. By means of this reaction it is therefore possible to convert oximidonaphthol into its isomeride.

N. H. M.

Intramolecular Change of Phenanthraquinonemonoxime. By P. WEGERHOFF (*Ber.*, **21**, 2355—2357).—*Diphenimide*,



is formed when phenanthraquinonemonoxime is treated with hydro-

chloric acid according to Beckmann's method (this vol., p. 43). It crystallises in colourless needles, melts at 215° , and is readily soluble in water, but only sparingly in alcohol.

Diphenamic acid, obtained by treating the imide with water, melts at $187-188^{\circ}$, and is soluble in hot water.

Diphenamide, prepared by acting on the imide with ammonia, loses ammonia when heated, and melts at the same temperature as the imide; it is soluble in water.

Diphenyleneketonecarboxylamide, $C_6H_4 < \text{CO} > C_6H_3 \cdot CONH_2$, is obtained when phenanthraquinonemonoxime is heated with concentrated sulphuric acid. It crystallises from absolute alcohol with $\frac{1}{2}$ mol. alcohol, in slender, silky needles, melting at 225° . This compound is also formed when the chloride of diphenyleneketonecarboxylic acid is treated with anhydrous ammonia, or when diphenimide is warmed with concentrated sulphuric acid. Phenanthraquinonemonoxime also undergoes intramolecular change when treated with phosphorus pentachloride, acetic chloride, or acetic anhydride.

F. S. K.

Anthracene Hydride. By L. LUCAS (*Ber.*, **21**, 2510—2511).—*Perhydroanthracene*, $C_{14}H_{24}$, is obtained by heating pure anthracene (1.5 gram) with an equal weight of amorphous phosphorus and hydriodic acid, sp. gr. = 1.7 (8 grams), for 12 hours at 250° . It crystallises in colourless plates, melts at 88° , boils at about 270° , and is readily soluble, except in water; it distils readily with steam. Bromine dissolved in carbon bisulphide scarcely acts on it.

When, in the reduction of anthracene, the heating is only continued for 5 to 6 hours, two hydrocarbons, probably of the formula $C_{14}H_{20}$, are obtained. The one is crystalline and melts at 52° , the other is an oil.

N. H. M.

Derivatives of Dianthranyl. By H. SACHSE (*Ber.*, **21**, 2512—2514).—*Dianthranyl tetrahydride*, $CH_2 < \text{C}_6H_4 > CH \cdot CH < \text{C}_6H_4 > CH_2$, is obtained by boiling dianthranyl (2 grams) with 4 per cent. sodium amalgam (150 grams) for some hours. It crystallises from benzene in prismatic needles melting at $248-249^{\circ}$, and dissolves rather sparingly in alcohol, readily in hot benzene. Bromine acts on it with formation of dibromanthracene. When dianthranyl is heated with hydriodic acid and phosphorus at 200° , anthracene dihydride (m. p. 106°) is formed.

Dibromodianthranyl, $C_{28}H_{18}Br_2$, is formed when bromine, diluted with glacial acetic acid, is slowly added to a boiling solution of dinitrodianthranyl in glacial acetic acid. It crystallises in lemon-coloured plates, rather easily soluble in benzene. It melts much above 300° .

Dichlorodianthranyl, $C_{28}H_{18}Cl_2$, obtained by heating dinitrodianthranyl with hydrochloric acid (sp. gr. = 1.19) at 180° , crystallises from glacial acetic acid in matted needles of a golden lustre which do not melt below 300° . It is rather readily soluble in benzene, sparingly in glacial acetic acid, very sparingly in alcohol. The solutions show a

blue fluorescence. Both the bromo- and the chloro-derivatives are sensitive to light. N. H. M.

Derivatives of Anthranol. By F. GOLDMANN (*Ber.*, 21, 2505—

2508).—*Ethoxyethylanthranyl*, $C_6H_4 \begin{smallmatrix} C(OEt) \\ | \\ C_{Et} \end{smallmatrix} C_6H_4$, is formed as a third product in the reaction between ethyl iodide, potash, and anthranol (this vol., p. 714), and is separated by means of the picrate. It crystallises from dilute alcohol in pale yellow, slender needles, melts at 77° , and dissolves very readily in benzene, light petroleum, and ether; the solutions show a blue fluorescence. The *picrate* forms reddish-brown needles. When ethoxyethylanthranyl is oxidised with chromic acid, Liebermann's ethyloxyanthranol is formed. The presence of anthranol can be shown by adding diazobenzenesulphonic acid to the dilute alkaline solution, when the solution acquires an intense blue colour. The dye may be recovered by converting it into the lead salt, which is then decomposed by hydrogen sulphide; it is obtained as a red, amorphous mass, readily soluble in water, with orange colour. N. H. M.

Derivatives of Anthranol. By F. HALLGARTEN (*Ber.*, 21, 2508—2510).—*Dimethylanthrone*, $C_6H_4 \begin{smallmatrix} CO \\ | \\ CMe_2 \end{smallmatrix} C_6H_4$, is prepared by boiling anthranol (12 grams) with potash (12 grams), water (60 c.c.), and methyl iodide (40 grams) for $3\frac{1}{2}$ hours in a reflux apparatus. The red oil is washed, boiled with water, and extracted with ether, from which it is precipitated by light petroleum. It crystallises in pale yellow, clear crystals, melts at $93-94^\circ$, dissolves readily in benzene and ether, sparingly in light petroleum.

Dimethylanthrane hydride, $C_6H_4 \begin{smallmatrix} CH_2 \\ | \\ CMe_2 \end{smallmatrix} C_6H_4$, obtained by heating the dimethylanthrone with hydriodic acid (sp. gr. 1.7) and amorphous phosphorus at $140-150^\circ$, is a white, crystalline substance which melts at 56° and dissolves in ether, benzene, and glacial acetic acid.

Dibenzylanthrone, $C_6H_4 \begin{smallmatrix} CO \\ | \\ C(C_6H_5)_2 \end{smallmatrix} C_6H_4$, is formed when anthranol (1 part) is heated with aqueous potash (1 part of potash in 5 parts of water) and benzyl chloride (2 parts). It crystallises from benzene in lustrous, white crystals, melting at 217° ; it is insoluble in light petroleum and alkalis, sparingly soluble in benzene. When reduced with hydriodic acid and amorphous phosphorus at 190° , the *hydride*, $C_6H_4 \begin{smallmatrix} CH_2 \\ | \\ C(C_6H_5)_2 \end{smallmatrix} C_6H_4$, is obtained. This forms slender, white crystals, readily soluble in ether, less so in benzene and alcohol; it melts at 115° .

Amylhydroanthrone, $C_6H_4 \begin{smallmatrix} CO \\ | \\ CH(C_5H_{11}) \end{smallmatrix} C_6H_5$, is obtained by boiling anthranol (10 grams), potash (10 grams), water (50 c.c.), and amyl iodide (44 grams), for eight hours in a reflux apparatus. It forms

yellowish crystals, melts at 252—253°, dissolves readily in ether, sparingly in alcohol and light petroleum. The dilute solutions show a blue fluorescence. N. H. M.

Spectra of the Alkoxy-anthraquinones. By C. LIEBERMANN (*Ber.*, 21, 2527).—The following numbers show the wave-lengths in millionths of a mm., and were obtained with solutions in cold concentrated sulphuric acid:—

Alizarin	605	493	
Alizarin ethyl ether..	598	487	
Anthraflavic acid.....	495	463	
Dimethyl salt.....	501	473	(437 very feeble)
Diethyl salt	504	477	(439 ")
Quinizarin.....	551	509	(483 feeble)
Monethyl salt	564	520	(484 ")
Diethyl salt	577	535	(494 ")
Isoanthraflavic acid....	—	540	(494 not sharp)
Diethyl salt	—	505	(492 ")
Flavopurpurin	533	495	
Diethyl salt	542	501	
Anthragallol.....	525	492	
Monethyl salt	—	515	(not sharp)
Diethyl salt	—	515	(")
Rufigallic acid	576	532	
Triethyl salt.....	579	545	

(Compare Liebermann and Jellinek, this vol., p. 715.)

N. H. M.

A New Dihydranzanthraquinone: Hystazarin. By C. LIEBERMANN (*Ber.*, 21, 2501—2502).—See next Abstract.

Hystazarin. By A. SCHOELLER (*Ber.*, 21, 2503—2505).—*Hystazarin* (dihydroxyanthraquinone), $[(OH)_2 = 2 : 3]$, is prepared by heating catechol (5 grams), phthalic anhydride (6.5 grams), and strong sulphuric acid (75 grams), at 140—150° for $4\frac{1}{2}$ to 5 hours; the product is poured into water (750 c.c.), heated to boiling and filtered hot. The precipitate is extracted with boiling water, dissolved in dilute potash and precipitated with acid. It is then dried on tiles, extracted with alcohol, and the solution evaporated. The orange-yellow mass which separates is dried and extracted with boiling benzene, which removes the small amount of alizarin formed in the reaction. The undissolved portion is recrystallised from acetone. Hystazarin forms orange-yellow, slender needles, soluble in hot alcohol, ether, and glacial acetic acid, almost insoluble in benzene; it does not melt at 260°. Alkalis dissolve it with a cornflower blue, ammonia with a violet, and strong sulphuric acid with blood-red coloration. The *barium* and *calcium* salts are blue and violet respectively. It gives a green coloration with ferric chloride. It dyes mordants only slightly. The absorption-spectrum of the sulphuric acid solution shows no bands but only a one-sided absorption. The dilute soda solution is blue, and shows an absorption of red, yellow,

and violet; on diluting, a band appears in the yellow part of the spectrum, which separates on further dilution into two bands: $\lambda = 619\cdot8$, $\lambda_1 = 587\cdot4$. The *diacetyl-derivative*, $C_{14}H_8O_2(OAc)_2$, crystallises in yellow needles melting at $205-207^\circ$. When hystazarin is reduced with zinc-dust, it is converted into anthracene. N. H. M.

Purification of Flavopurpurin. By G. JELLINEK (*Ber.*, **21**, 2524—2526).—500 grams of the powdered technical product is suspended in about 3 litres of water, made alkaline with potash and filtered. The solution is diluted with water to 15 litres, heated to boiling in an open vessel, and a solution of lead acetate added until a sample of the filtered liquid gives a precipitate on the further addition of lead acetate, which becomes of a light leather colour, after carbonic anhydride is passed through. The precipitated lead compound is filtered through a bag, the bag tied up and boiled repeatedly with water in a copper vessel until the water has only a light rose colour. The contents of the bag are now decomposed by sulphuric acid and separated from lead sulphate by means of moderately dilute alcohol. The alcoholic solution is evaporated down, the first separation removed, and the rest left to crystallise.

In purifying small amounts of the technical product (50 grams and less), an alcoholic-alkaline solution is used for the precipitation of the lead compound.

The red filtrate from the lead compound yields splendid ruby-coloured needles, which, when treated with acid become converted into a mass of yellow needles of dihydroxyanthraquinone.

N. H. M.

Terpenes and Ethereal Oils. By O. WALLACH (*Annalen*, **246**, 221—239).—The oil obtained from the needles of *Pinus picea* and of other species of pines consists chiefly of pinene (lævogyrate), and also contains a considerable quantity of *limonene*, which is a physical isomere of the limonene contained in cummel oil and in the oil from orange-peel. This variety of limonene boils at $175-176^\circ$. Its sp. gr. at 20° is $0\cdot846$. It is lævogyrate, $[\alpha]_D = -105^\circ$. The index of refraction for the sodium line is $1\cdot47459$ at 20° .

The *tetrabromide*, prepared by acting on a mixture of the limonene with glacial acetic acid, melts at 104° , and resembles the ordinary tetrabromide in crystalline form, but differs from it in its action on polarised light, as it is lævogyrate. The nitrosochloride from the lævogyrate limonene only differs from the ordinary limonene nitrosochloride by being lævogyrate.

Dipentene is formed by mixing together lævo- and dextro-limonene in equal quantities. By brominating this mixture, dipentene tetrabromide is obtained. This compound can also be prepared by mixing in equal quantities dextro- and lævo-limonene tetrabromides. Lævogyrate limonene nitrosochloride, on decomposition with alcoholic potash, yields dextrogyrate carvoxime melting at 72° . Isonitrosodipentene, which melts at 93° and is optically inactive, is produced when equal quantities of + and — carvoxime are mixed.

Isonitrosodipentene and dextrocarvoxime have identical molecular weights, according to the determinations made by Raoult's method.

The phellandrene from *Phellandrium aquaticum* and many other plants is dextrogyrate, but that from *Eucalyptus amygdalina* is lævogyrate. The nitrites from the two isomerides melt at 103°, and appear to be identical in their properties. The dextrophellandrene yields a lævogyrate nitrite, and the lævophellandrene yields a dextrogyrate nitrite. An optically inactive modification is obtained by mixing the nitrites in equal quantities. W. C. W.

Terpenes and Ethereal Oils. By O. WALLACH and E. GILDMESTER (*Annalen*, **246**, 265—284).—*Cineolic acid*, $C_{10}H_{16}O_5$, is prepared by oxidising cineol with potassium permanganate. The filtered solution is evaporated to dryness and the residue extracted with alcohol, which dissolves out potassium cineolate, from which the acid is easily isolated. Cineolic acid is soluble in 70 parts of water at 15°, and in 15 at 100°. It is more soluble in warm alcohol and ether. The calcium salt, $CaC_{10}H_{14}O_5 + 4H_2O$, is insoluble in boiling water, but dissolves slowly in cold water. The ethyl salt boils at 155° under 11 mm. pressure. Cineolic acid melts at 196° with decomposition. On oxidation with potassium permanganate, it yields oxalic and carbonic acids.

The oil of *Eucalyptus amygdalina* contains cineol and phellandrene. It is lævogyrate, boils between 165—180°, and its sp. gr. is 0.855 at 18°. This phellandrene is a physical isomeride of the phellandrene contained in *Phellandrium aquaticum* (see preceding Abstract). The hydrocarbon eucalyptene from *Eucalyptus globulus* is identical with dextropinene. W. C. W.

Chemistry of Buchu Leaves. By Y. SHIMOYAMA (*Arch. Pharm.* [3], **26**, 403—417).—Flückiger obtained from the oil of buchu leaves a peculiar compound, described under the name of diosphenol; it forms colourless crystals belonging to the monoclinic system, which can be obtained several centimetres long by sublimation. It is easily soluble in alcohol, less so in ether, and scarcely at all in water. Its solutions are neutral. Diosphenol dissolves in concentrated sulphuric acid; on saturating the solution with barium carbonate and evaporating the filtrate, a little amorphous barium salt is obtained. According to Spica, diosphenol is an oxycamphor of the composition $C_{10}H_{16}O_2$; the author's results confirm this. *Methyldiosphenol*, obtained by the action of potassium hydroxide and methyl iodide on diosphenol, is a colourless liquid which boils at 232—235°, and has a sp. gr. of 0.985 at 15°. It is easily soluble in alcohol and ether, but not in water. Its composition is $C_{10}H_{15}O_2Me$. The corresponding *ethyl*-compound is also a colourless liquid insoluble in water, easily soluble in alcohol and ether, of sp. gr. 0.967 at 15°. Boiling point 270—272°. *Acetyldiosphenol* is obtained by mixing diosphenol with anhydrous sodium acetate and excess of acetic anhydride, and heating at 145° in a closed tube. The rectified product is a colourless, odourless liquid which boils at 269—270°, although not without decomposition. Sp. gr. 1.032 at 20°; easily soluble in alcohol and ether but not in water. The compound is neutral, but after rectification has an acid reaction.

Long digestion of diosphenol with alcoholic potash partly converts it into *diolic acid*; this is separated from the liquid residue in the retort by the addition of hydrochloric acid, dissolved in ammonium carbonate, treated with animal charcoal, and precipitated with acid. Diolic acid forms white, crystalline needles; its aqueous solution has an acid reaction; it neutralises strong bases and liberates carbonic anhydride from carbonates. It melts at $96-97^{\circ}$, volatilises slowly on the water-bath, and decomposes when heated strongly, evolving a menthol-like odour. It is soluble in 122.7 parts of water at 18° , and in 82 parts at 100° ; easily soluble in alcohol, ether, chloroform, benzene, and carbon bisulphide. Its composition is $C_{10}H_{18}O_3 + H_2O$. The barium salt, $(C_{10}H_{17}O_3)_2Ba + 5H_2O$, is soluble in 67.89 parts water at 17.5° and 19.7 parts at 100° , and also in alcohol. Over sulphuric acid, it gradually loses its water of crystallisation. The white, amorphous silver salt, $C_{10}H_{17}O_3Ag$, rapidly blackens on exposure to the light. It is scarcely soluble in water even at 100° . The sodium and ammonium salts are amorphous. The calcium and magnesium salts are white, amorphous powders insoluble in water, whilst the strontium salt is easily soluble. The copper salt is light-brown, the iron salt red-brown; both are only slightly soluble in water. Diosphenol when fused with potassium hydroxide yielded an acid agreeing in every particular with diolic acid, but melting at 86° , that is 10° lower; attempts to raise the melting point of the new acid by recrystallisation were unsuccessful.

Reduction of diosphenol in alcoholic solution by means of sodium amalgam gave an oily substance, which was dissolved in aqueous ether and treated with sodium to reduce the diosphenol still remaining unacted on. The solution was then allowed to evaporate, when an oily liquid permeated with crystals was left. The crystals, prismatic in form, melt at 159° , are odourless, sparingly soluble in alcohol and ether, and the alcoholic solution does not give the dirty-green coloration with ferric chloride solution which diosphenol does. Its composition is $C_{10}H_{16}O_3$, and must be considered as the *diol alcohol*. The oily compound occurring with these crystals is probably $C_{10}H_{18}O$, the principal component of buchu oil, according to Flückiger, and described by Spica under the name of diosmeleoptene. Diosphenol dissolved in carbon bisulphide and treated with bromine gives fine yellow crystals of the composition $C_{10}H_{14}Br_2O_2$; these melt at 43° , and are soluble in alcohol and ether, but not in water.

J. T.

Apiole. By J. GINSBERG (*Ber.*, **21**, 2514—2516; compare this vol., p. 722).—*Tribromapiole*, $C_{12}H_{11}Br_3O_4$, is prepared by slowly adding bromine (2 parts) dissolved in carbon bisulphide to a cooled solution of apiol (1 part) in carbon bisulphide. The crystalline mass obtained by evaporating the carbon bisulphide is washed with dilute alcohol and recrystallised from absolute alcohol, from which it separates in flat needles melting at $88-89^{\circ}$. It is readily soluble in most solvents except water. The solution in strong sulphuric acid is violet.

Tribromisapiole, $C_{12}H_{11}Br_3O_4$, is prepared in a manner similar to the compound just described, except that glacial acetic acid is used as the

solvent. It crystallises from glacial acetic acid in colourless, lustrous plates, melts at 120° , and resembles its isomeride in solubility.

A *chlorine-derivative* of the formula $C_{12}H_{12}O_4Cl_2$, or $C_{12}H_{14}O_4Cl_2$, was obtained by boiling a solution of isapiole in benzene with phosphorus pentachloride: it crystallises in small prisms. No crystalline chlorinated compound could be obtained from apiole.

When the nitro-derivative of apiole, previously described, is dissolved in 20 parts of bromine, the compound $C_{10}H_8Br_4O_2$ is formed. This crystallises from absolute alcohol in thin plates of a silvery lustre, melts at 159° , and is soluble in the usual solvents, except water. Isapiole, when oxidised with manganese peroxide and sulphuric acid, yields an acid melting at 250° , not identical with that obtained by Ciamician and Silber.

N. H. M.

Methysticin. By D. DAVIDOFF (*J. Russ. Chem. Soc.*, 1887, 522—523).—The author has studied the properties of methysticin from the root of Kawa-Kawa, or *Macropiper methysticum*, and some of its derivatives. It melts at 138 — 139° , and has the formula $C_{16}H_{18}O_6$. The diacetyl-derivative, $C_{20}H_{22}O_7$, melts at 122 — 123° , the dibenzoyl-compound, $C_{30}H_{28}O_7$, melts at 148° , the hydrate $C_8H_{10}O_3$ melts at 158 — 159° , the ethyl ether, $C_8H_9EtO_3$, melts at 99 — 100° , benzoylmethysticin acid, $C_{15}H_{14}O_4$, melts at 122° , and the amido-compound $C_8H_{11}NO_2$, forms yellow crystals.

B. B.

α - γ -Dimethylparatoluquinoline. By W. PFITZINGER (*J. pr. Chim.* [2], 38, 40—48).— α - γ -Dimethylparatoluquinoline,



is prepared as follows:—A mixture of 30 grams of paraldehyde with 40 grams of acetone is saturated in the cold with hydrogen chloride, kept for about 12 hours in a freezing mixture, then poured into a mixture of 65 grams of paratoluidine with 130 grams of fuming hydrochloric acid and heated for 6 to 8 hours, the whole being frequently shaken; the product is diluted with water, boiled to expel neutral compounds, saturated with alkali and distilled with steam. The mixture of bases in the distillate is dissolved in alcohol, precipitated with an alcoholic solution of picric acid, the picric compound decomposed with soda, and the free base distilled with steam.

It is sparingly soluble in water, and separates from the hot aqueous solution in the form of an oil which solidifies to slender, colourless needles melting at 63 — 64° . The crystals contain water which they lose in a desiccator but absorb again on exposure to the air. It is readily soluble in alcohol, ether, benzene, acetone, chloroform and light petroleum, and crystallises from 50 per cent. alcohol in needles which probably contain alcohol. The anhydrous base, which is somewhat difficult to obtain, boils at 277 — 278° , and on cooling, the greater portion solidifies to a mass of deliquescent plates which after exposure to the air melt at 63 — 64° . It has a sweetish smell, a sharp, bitter taste and is not acted on by nitrous acid.

The *sulphate*, $C_{12}H_{13}N, H_2SO_4 + H_2O$, crystallises from boiling

alcohol in colourless needles or large, rhombic forms which lose their water at 100—110°. The anhydrous salt is readily soluble in water but only sparingly in cold alcohol, and melts at 221—222° when heated quickly. The *hydrochloride*, $C_{12}H_{13}N \cdot HCl + 2H_2O$, crystallises in colourless needles, loses its water at 100—110°, and is very readily soluble in alcohol and hot water. It does not melt when heated to 240°. The *platinochloride*, $2C_{12}H_{13}N \cdot H_2PtCl_6 + 2H_2O$, forms bright-yellow needles, and is very sparingly soluble in water, but almost insoluble in alcohol and ether. It loses its water at 125—130°; the anhydrous salt is hygroscopic. The *dichromate*, $2C_{12}H_{13}N \cdot H_2Cr_2O_7$, crystallises from hot water in long, red needles, is sparingly soluble in cold water, and decomposes gradually above 150°. The *picrate*, $C_{12}H_{13}N \cdot C_6H_3N_3O_7$, crystallises from hot alcohol or hot acetone in greenish-yellow needles which melt at 200—201° if heated quickly.

The *methiodide*, $C_{12}H_{13}N \cdot MeI + H_2O$, prepared by dissolving the base in methyl iodide, crystallises from hot water in slightly coloured, shining needles, which lose their water at 100—110° and melt at 225—226° when heated quickly. It is readily soluble in alcohol and water, but insoluble in ether. Compare Combes (*Compt. rend.*, **106**, 142—145; this vol., p. 504). F. S. K.

A β -Lactone of the Quinoline Series. By A. EINHORN and P. LEHNERING (*Annalen*, **246**, 160—179).—The best yield of quinolylacrylic acid is obtained by the action of alcoholic potash or soda on the condensation product of chloral and quinaldine, trichloro- α -hydroxypropylquinoline, $C_9NH_5 \cdot CH_2 \cdot CH(OH) \cdot CCl_3$. 250 grams of a 20 per cent. solution of potassium hydroxide in alcohol and 50 grams of the condensation product are brought into a flask of 5 litres capacity. The mixture is placed on the water-bath. As soon as a lively reaction begins, the flask is removed and the contents are agitated. The heat produced by the reaction causes the greater part of the alcohol to evaporate and potassium quinolylacrylate remains in solution. The free acid is prepared from the potassium salt in the usual way by decomposition with hydrochloric acid.

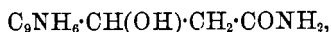
Trichloropropenylquinoline, $C_9NH_5 \cdot CH : CH_2 \cdot CCl_3$, is prepared by gradually adding phosphorus pentachloride to trichloro- α -hydroxypropylquinoline and chloroform and heating the mixture. The chloroform is removed by evaporation and the residue is poured into water. On recrystallisation from ethyl acetate, the trichloropropenylquinoline forms prismatic plates which melt at 145°.

Quinolylacrylic acid dissolves in acetic acid saturated with hydrogen bromide. The operation is carried on in sealed tubes at 100°. On cooling, the solution deposits crystals of the *hydrobromide of quinolyl- β -bromopropionic acid*, $C_9NH_5 \cdot CHBr \cdot CH_2 \cdot COOH \cdot HBr$. This compound is decomposed by alkaline carbonates, yielding quinolyl- β -lactic acid and the corresponding lactone if the solution is cold, or quinolylethylene with a hot solution. The *lactone of quinolyl- β -hydroxypropionic acid*, $C_9NH_5 \cdot CH < \begin{smallmatrix} CH_2 \\ -O- \end{smallmatrix} > CO$, crystallises in needles, melts at 83° and decomposes at 100°. It is soluble in abso-

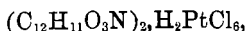
lute alcohol, benzene and ether, and forms crystalline salts with picric, hydrochloric, and sulphuric acids. It is converted into the quinolyl- β -lactic acid by the action of caustic alkalis, and into the corresponding amide by the action of alcoholic ammonia.

Quinolylethylene, $C_9NH_5 \cdot CH:CH_2$, is an oily liquid volatile in a current of steam and slightly soluble in water. The *platinochloride*, $(C_{11}H_9N)_2, H_2PtCl_6 + 4H_2O$, forms orange-coloured needles and melts at $186-187^\circ$. The *aurochloride*, $C_{11}H_9N, HAuCl_4$, crystallises in yellowish-red needles. It melts at $158-159^\circ$.

A solution of the hydrobromide of quinolyl- β -bromopropionic acid, in excess of ammonia, deposits *quinolylactamide*,



in white crystals. The base melts at $151-152^\circ$. By boiling with hydrochloric acid, it is converted into the hydrochloride of *quinolyl- β -lactic acid*, $C_9NH_5 \cdot CH(OH) \cdot CH_2 \cdot COOH$. This salt crystallises in thick prisms and melts at $187-188^\circ$. The *platinochloride*,



forms yellowish-red prisms. It melts at 218° with decomposition. Quinolylactic acid is obtained in large, colourless prisms by covering the acid with hot chloroform, then adding methyl alcohol until the acid dissolves, and evaporating the solution. The acid melts at 176° and is soluble in methyl alcohol, ethyl alcohol, and ethyl acetate. The sodium salt exists as a jelly and also as a crystalline powder. The *methyl* salt melts at 62° , crystallises in transparent prisms, and dissolves in benzene, alcohol, and ethyl acetate. W. C. W.

Opianic Acid. By A. BISTRZYCKI (*Ber.*, **21**, 2518-2524).—*Diphenylhydrazonopianic acid*, $C_{22}H_{20}N_2O_4$, is obtained by adding an aqueous solution of diphenylhydrazine hydrochloride (1 mol.) containing a trace of hydrochloric acid to a concentrated, boiling aqueous solution of opianic acid (1 mol.) and sodium acetate (1 mol.), and boiling the mixture for a few minutes. It forms yellow crystals, melts at $171-172^\circ$, dissolves readily in hot alcohol, chloroform, acetone and benzene, but is almost insoluble in light petroleum. Dilute alkali solutions dissolve it readily. The *calcium* salt with 8 mols. H_2O crystallises in plates.

Diphenylhydrazonenitropianic acid, $C_{22}H_{19}N_3O_6$, is prepared in a manner similar to the opianic acid derivative, except that twice the amount of sodium acetate is used; it crystallises in small, lustrous, orange-coloured prisms, melts at 217° , dissolves readily in hot acetone, chloroform, glacial acetic acid and alcohol, sparingly in benzene and ether, and is insoluble in light petroleum. The *calcium* salt forms red, microscopic needles.

Opianylhydrazobenzene, $C_{22}H_{20}N_2O_4$, is formed when hot, concentrated alcoholic solutions of opianic acid and hydrazobenzene are mixed and boiled for a few minutes. It crystallises in white plates, melting at $186-188^\circ$, and is rather soluble in hot alcohol, acetone, and chloroform, almost insoluble in ether and light petroleum.

Benzidylopianic acid, $C_{32}H_{28}N_2O_6$, obtained from opianic acid

(2 mols.) and benzidine (1 mol.), crystallises in microscopic needles, is almost insoluble in the usual solvents, and does not melt at 230° ; it can be crystallised from boiling nitrobenzene. Hot soda solution dissolves it readily.

Opiancarbamide, $C_{11}H_{12}O_5N_2$, crystallises in groups of needles, melts at 259° with decomposition, dissolves sparingly in hot alcohol, and is almost insoluble in other solvents. Hot aqueous sodium carbonate and cold potash dissolve it readily.

Toluyleneopiamine, prepared from opianic acid, metaparabenzylene-diamine hydrochloride and sodium acetate, crystallises in small needles, melts at $242-243^{\circ}$, dissolves rather readily in boiling glacial acetic acid, acetone, and chloroform, but is almost insoluble in water, cold alcohol, and benzene. Acids and alkalis dissolve it readily.

N. H. M.

Isatropylcocaine. By C. LIEBERMANN (*Ber.*, **21**, 2342—2355; compare Hesse, *Abstr.*, 1887, 1126).—An alkaloid which the author names isatropylcocaine is present in the mixture of amorphous alkaloids obtained as a bye-product in the preparation of cocaine.

Isatropylcocaine, $C_{12}H_{23}NO_4$, is prepared in the pure state as follows: the yellow, sticky, amorphous mixture is dissolved in hydrochloric acid and the filtered solution extracted with ether. The extract contains considerable quantities of benzaldehyde. The solution is freed from ether by means of a stream of air and the base precipitated fractionally with alkali. It is then obtained in the form of a white, chalky, amorphous powder, the quantity of which is about 70 per cent. of the crude material. The middle fractions are dissolved in hydrochloric acid, again fractionally precipitated with soda, extracted with light petroleum to remove traces of cocaine, and dried in a stream of air for several days at the ordinary temperature, and finally at 45° .

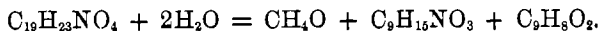
The alkaline filtrate from the alkaloid contains ecgonine, the quantity of which is from 1 to 2 per cent. of the crude material.

Isatropylcocaine is very similar to cocaine, but both the base and its salts are amorphous, and the former is not so readily soluble in ammonia and light petroleum as cocaine. It is easily soluble in cold alcohol, ether, benzene, and chloroform, but only very sparingly in light petroleum, and in all cases a resinous mass is obtained when the solvent is evaporated. It begins to soften at 65° , but has no definite melting point; at $90-100^{\circ}$ it loses water slowly, and at 120° it turns brown and is gradually decomposed. All the salts are amorphous and soluble in water. Picric acid produces a yellow, chromic acid an orange, and potassium permanganate a violet precipitate, which changes to brown. The chlorides of mercury, tin, gold, and platinum and most of the usual reagents for alkaloids also give amorphous precipitates. The alcoholic solution does not show an alkaline reaction with phenolphthalein, and is dextrorotatory.

The base is a powerful poison, but its action is not similar either to that of cocaine or atropine; the symptoms of poisoning sometimes observed after the administration of impure cocaine may be due to this alkaloid.

Methyl chloride is evolved when the base is heated with con-

centrated hydrochloric acid, and when boiled with strong hydriodic acid methyl iodide is obtained, the quantity of which, estimated by Zeisel's method, showed that one methyl-group has been eliminated. It is also decomposed, with separation of methyl alcohol, when heated for a long time with dilute sulphuric acid, but no ethyl alcohol is formed. When boiled for about an hour with hydrochloric acid, sp. gr. 1.1, it is decomposed into methyl alcohol, ecgonine, and isotropic acid in molecular proportion as in the following equation :



The product of the reaction is filtered and the two isotropic acids in the residue separated by means of their barium salts.

γ-Isotropic acid, $\text{C}_9\text{H}_8\text{O}_2$, forms about two-thirds of the residue. It crystallises from 50 per cent. alcohol in small, colourless needles, melts at 274° , and is soluble in hot glacial acetic acid, but only very sparingly in ether, benzene, and carbon bisulphide. The *barium* salt, $(\text{C}_9\text{H}_7\text{O}_2)_2\text{Ba}$, is crystalline, and readily soluble in water. The *calcium*, *copper*, and *silver* salts are soluble in water. The ethyl- and methyl-derivatives are very readily formed when hydrogen chloride is passed into a solution of the acid in the corresponding alcohol. The *ethyl* salt, $\text{C}_9\text{H}_7\text{EtO}_2$, is insoluble in ammonia and sparingly soluble in alcohol, from which it crystallises in needles melting at 146° . *Methyl γ-isotropate*, $\text{C}_9\text{H}_7\text{MeO}_2$, crystallises in plates or needles, melts at 174° , and distils at about 300° with very slight decomposition, but has no constant boiling point. A vapour-density determination in anthracene vapour showed that it is at first polymeric, and is only completely transformed into the simple molecule after about half an hour's heating.

δ-Isotropic acid, $\text{C}_9\text{H}_8\text{O}_2$, forms about one-third of the residue. It is more easily soluble in water than the *γ*-acid, and melts at 206° . Neither this nor the *γ*-acid yields benzaldehyde when oxidised with potassium permanganate or chromic acid. An aqueous solution of the ammonium salt gives precipitates with calcium chloride, mercuric chloride, and copper acetate. The *barium* salt, $(\text{C}_9\text{H}_7\text{O}_2)_2\text{Ba}$, is sparingly soluble in water. The *silver* salt, $\text{C}_9\text{H}_7\text{O}_2\text{Ag}$, is amorphous but becomes crystalline when boiled with water. The *ethyl* salt, $\text{C}_9\text{H}_7\text{EtO}_2$, is a viscid oil; it has no constant boiling point, but after boiling for a long time it distils at $264\text{--}270^\circ$, and condenses to a colourless, mobile oil. The *methyl* salt, $\text{C}_9\text{H}_7\text{MeO}_2$, crystallises from dilute alcohol in prisms or needles, melts at 76° , and is readily soluble in all solvents except water. A vapour-density determination in anthracene vapour showed that it is at first polymeric, but, the transformation into simple molecules takes place much more quickly than is the case with the corresponding salt of the *γ*-acid.

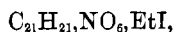
The acids described above are very similar in appearance and solubility to *α*-isotropic acid (Lossen, *Annalen*, **138**, 235), *β*-isotropic acid (Fittig, *Annalen*, **206**, 34), and the isotropic acids which the author has previously obtained from atropine, but they are not identical with any of these compounds. *β*-Isotropic acid seems to be formed when hydrogen chloride is passed into a methyl alcoholic solution of *α*-isotropic acid. *Methyl β-isotropate* melts at 91° .

The molecular weight of δ -isatropic acid, methyl and ethyl δ -isatropate, and methyl and ethyl γ -isatropate was determined by Raoult's method in glacial acetic acid solution, and in all cases the results agreed for the molecular formulæ given above; the salts are all reprecipitated unchanged when water is added to the glacial acetic acid solution. The acid filtrate from the atropic acids (see above) contains ecgonine and a very small quantity of a complex mixture of acids consisting principally of δ -isatropic acid, but in which benzoic acid was recognised. Anhydroecgonine is also sometimes present. The quantities of ecgonine and isatropic acids are approximately in accordance with the equation given above.

Boiling baryta decomposes the amorphous alkaloïd in a similar manner to hydrochloric acid, but the ecgonine is partially decomposed.

Other bases occurring with cocaïne also yield ecgonine when treated with acids. The author has succeeded in preparing benzoylecgonine from ecgonine. F. S. K.

The Berberine Alkaloids. By E. SCHMIDT and F. WILHELM (*Arch. Pharm.* [3], **26**, 329—365; compare *Abstr.*, 1885, 675; 1886, 633, 1041; 1887, 174, 383, 505, 1057).—*Hydrastine*. By Wilhelm.—The extract obtained by treating the coarsely powdered root of *Hydrastis canadensis* with water acidified with acetic acid at 100°, is evaporated to a syrup and excess of dilute sulphuric acid added, when berberine sulphate separates. The filtrate neutralised with ammonia gives a precipitate containing much hydrastine; this is separated, and on adding ammonia in excess to the filtrate a further precipitate is produced, which contains *canadine*. Both precipitates boiled with ethyl acetate give solutions which on cooling deposit hydrastine in large crystals, somewhat coloured, but rendered pure by recrystallisation. The crystals from the second ammonia precipitate are much purer than those from the first; by slow evaporation of the ethyl acetate solution they can be obtained as large as walnuts. *Hydrastine picrate*, $C_{21}H_{21}NO_6, C_6H_2(NO_2)_3.OH + 4H_2O$, is thrown down as an amorphous, yellow precipitate, which is deposited from its boiling alcoholic solution in splendid, yellow needles. By the action of ethyl iodide on hydrastine under pressure, a well-crystallised ethiodide,



can be obtained of the form $\infty P. \infty P^{\infty}. \dot{P}^{\infty} . (P. \dot{P}^{\infty})$, melting at 205° to 206°. The corresponding chloride could only be obtained in a gummy mass; its solution was therefore precipitated with platinum and gold chlorides respectively, and the corresponding double salts were obtained and analysed. Both are amorphous, the platinumchloride being light red, melting at 207°, and having the composition



and the aurochloride being yellow, melting about 110°, and having the composition $C_{21}H_{21}NO_6, EtCl, AuCl_3$. *Hydrastine-ethylammonium hydriodide*, obtained by exactly precipitating the iodine from hydrastine ethiodide by means of silver oxide, concentrating the filtrate, and

allowing to remain over sulphuric acid, appears as compact, slightly coloured crystals, which are purified by recrystallisation from hot water. Their composition is $C_{21}H_{21}NO_6Et.OH$, showing that the hydrastine has the character of a tertiary base, and does not, as Power supposed, belong to the imido-bases. The attempts to obtain a hydro-compound by the action of nascent hydrogen on hydrastine, both in acid and alkaline solution, were unsuccessful. The evidence as to the existence of a third alkaloid, canadine, was doubtful.

Action of Oxidising Agents on Hydrastine. By E. Schmidt and F. Wilhelm.—Hydrastine, when treated with manganese dioxide and sulphuric acid, yields opianic acid and *hydrastinine*. Oxidation with platinic chloride gives the same products. Potassium permanganate in alkaline solution produces hemipinic and nicotinic acids; in acid solution opianic acid is produced, as one of the authors had ascertained when Freund and Will's publication of the same fact first appeared. The base formed simultaneously was not isolated, but by employing barium permanganate hydrastinine in small quantity was obtained along with opianic acid. Chromic acid yielded the same two products.

Comparing narcotine and hydrastine, E. Schmidt considers that the former contains three methoxyl-groups, thus: $C_{19}H_{14}(OMe)_3NO_4$, whilst the latter contains only two, thus: $C_{19}H_{12}(OMe)_2NO_4$. Since the oxidation of narcotine with manganese dioxide and sulphuric acid yields opianic acid and cotarnine, and under the same conditions hydrastinine gives opianic acid and hydrastinine; further, as opianic acid contains two methoxyl-groups, and cotarnine contains one of these groups, as shown by Wright, it follows that hydrastinine contains no methoxyl-group, and cotarnine may prove to be a methylated hydrastinine. The author hopes later to succeed in converting hydrastine into narcotine. J. T.

The Acids of Pig's Bile. By S. JOLIN (*Zeit. physiol. Chem.*, **12**, 512—557).—In a former paper (see Abstr., 1887, 742) it was shown that in pig's bile there is, in addition to Strecker's hyoglycocholic acid, a second acid called β -hyoglycocholic acid. These two acids can be separated by fractional saturation with sodium sulphate of the bile from which the mucin has been removed. In the present paper, after a review of previous researches on the subject, the method of preparation of the bile and separation of the two acids is described in detail. The α -acid (Strecker's) is comparatively easily freed from impurities; but the β -acid and its salts are much more difficult to obtain pure. After a complicated process of solution and reprecipitation, the sodium salt of the β -acid was prepared fairly free from colouring matter; a crystalline substance of doubtful nature was next separated; and finally a number of only partially successful efforts were made to free it from admixture with hyotaurocholic acid, and small quantities of the α -acid or its salts. There are a large number of elementary analyses given of this compound in different stages of its purification; all attempts to prepare a crystalline compound from it were unsuccessful. The concluding pages of the paper give a list of the reactions of the acid, and of a number of its metallic salts, but

the value of such observations seems to be considerably discounted by the fact that the material under investigation is admitted to be impure.

W. D. H.

Lecithin. By E. GILSON (*Zeit. physiol. Chem.*, **12**, 585—602).—Diaconoff (*Centr. Med. Wiss.*, 1868) regarded lecithin as a compound of the nature of a salt of neurine, which played the part of the base with distearyl-glycerophosphoric acid. Strecker (*Annalen*, 1868), on the other hand, considered lecithin as an ether-like combination, the neurine being united to the acid by means of the oxygen of the hydroxyl. In favour of the latter view, Hundeshagen has stated that the neurine salt of distearyl-glycerophosphoric acid prepared synthetically has none of the properties of lecithin.

In the present research, lecithin was prepared with great care from yolk of egg, and the decomposition-products of the action on it of sulphuric acid of strengths varying from 10 to 50 per cent., and also of dilute alkalis (1 per 1000 to 5 per cent. sodium hydroxide solution), were investigated. It was found that sulphuric acid acts exceedingly slowly in decomposing lecithin, especially when the acid employed is of the lesser strength mentioned above. The products of the action are small quantities of glycerophosphoric acid, another phosphorus-containing substance (distearyl-glycerophosphoric acid?), and free phosphoric acid; the last-named is the most abundant. Dilute alkalis act more energetically than the acid; the chief product is glycerophosphoric acid.

These results certainly negative Diaconoff's theory that neurine plays the part of a base in a combination resembling a salt, and the conclusion is drawn that Strecker's is the correct view to take of the nature of lecithin.

W. D. H.

Physiological Chemistry.

Tension of Oxygen in the Blood, and in Solutions of Oxy-hæmoglobin. By G. HÜFNER (*Zeit. physiol. Chem.*, **12**, 568—584). —The part played by the partial pressure of oxygen in causing the dissociation of oxyhæmoglobin at the normal body temperature, is a problem which has not been fully worked out. Paul Bert has shown that the dissociation occurs more easily at 40° than at temperatures below that point. Frankel and Geppert obtained similar results, and the author has previously shown (*Zeit. physiol. Chem.*, **6**, 94) that besides pressure and temperature, another very important factor is the concentration of the solution of oxyhæmoglobin used. The present research was undertaken not only with fresh defibrinated blood of the ox and dog, but also with solutions of oxyhæmoglobin crystals from the ox, which are more readily obtained in larger quantities, and are also much more soluble than the dog's oxyhæmoglobin previously used. The apparatus used is fully described and figured. It consists of the

following parts:—(1.) A bulb apparatus, in which the blood or oxyhæmoglobin solution and the gases to be investigated can be collected separately, and subsequently mixed and shaken vigorously. (2.) A manometer by which the pressure of the gases before and after the admixture can be read off. There are also means by which the gases can be analysed; mixtures of oxygen and nitrogen were those always employed. (3.) The whole apparatus is immersed in a very large water-bath, and thus the temperature at which all the processes are carried out can be regulated and observed. Barometrical readings are also necessary for correcting the various readings.

A number of observations at 20° and 35° gave results which demonstrated that dissociation occurs more readily at the latter temperature than at the former. The following may be taken as examples:—

Partial Pressure of Oxygen in millimetres of Mercury.

	At 20°.		At 35°.	
	Before shaking.	After shaking.	Before shaking.	After shaking.
1	42·17	43·15	42·38	46·51
2	46·27	46·63	46·31	50·73
3	54·77	56·26	54·73	57·49

A similar table shows also that the volume of oxygen was increased by the vigorous admixture of the mixed gases with the solution of oxyhæmoglobin or blood to a much greater extent at 35° than at 20°.

Another series of observations in which the temperature remained approximately constant at 35°, and in which the pressure was varied, showed that at this temperature (34–35°) the limit was reached when dissociation of oxyhæmoglobin no longer took place, on increasing the partial pressure of oxygen to 62–82 mm. of mercury; this corresponds with about 300 mm. of atmospheric pressure.

The same figure approximately was obtained whether the oxyhæmoglobin was used in a pure condition dissolved in a 0·1 per cent. solution of sodium carbonate, or whether fresh defibrinated blood was employed. The solution in the former case contained 6 to 8 per cent. of oxyhæmoglobin.

One would naturally expect that at higher temperatures, for instance in the blood during fever, the conditions under which oxyhæmoglobin is dissociated would be different; but for healthy, warm-blooded animals, a fall in atmospheric pressure to below 300 mm. of mercury would be for physico-chemical reasons exceedingly perilous; such a pressure would be attained at a height of 5500 metres.

W. D. H.

Uric Acid in the Urine of Herbivora. By F. MITTELBACH (*Zeit. physiol. Chem.*, 12, 463–466).—No data existing as to the occurrence of uric acid in the urine of herbivorous animals, a number of specimens

of such urine were examined with the following results, Ludwig's method of separating uric acid being employed.

Urine of Oxen.—Twenty-three specimens were examined; they varied in sp. gr. from 1.033 to 1.0425, and as a rule the reaction was strongly alkaline. Phosphoric acid was present in 12, and absent or nearly so in 11 cases. Uric acid was also present; in six cases in which a quantitative analysis was made, the quantity present varied from 8 to 45 milligrams per 100 c.c. of urine. In the urine of seven cows, the results were similar; the sp. gr. was, however, less (1.005—1.011).

Urine of Sheep.—Seven specimens were examined; the sp. gr. varied from 1.010 to 1.0425; the reaction was alkaline; uric acid was present; phosphoric acid was present in traces in two cases only.

Urine of Horses.—Five specimens were examined; all gave an abundant sediment of calcium carbonate; all were strongly alkaline, and had an average sp. gr. of 1.045. Uric acid was present, and phosphoric acid absent in all the specimens.

Urine of Pigs.—Nine specimens were examined; the results were somewhat different from the preceding, the pig being omnivorous; the reaction was acid; the sp. gr. 1.006—1.032; phosphoric acid was present in all cases; so also was uric acid (3—30 milligrams per 100 c.c. of urine).

W. D. H.

Influence of Atropine on Salivary Secretion. By J. N. LANGLEY (*J. Physiol.*, 9, 55—64).—Atropine when administered to animals, causes a stoppage of the secretion of saliva; stimulation of the nerves going to the glands no longer causes the formation of saliva to take place. In a normal condition, stimulation of different nerves causes the formation of saliva of different kinds, differing, that is to say, in the proportion of solids to water. From this and similar experiments it has been concluded that the different nerve-fibres have different functions, and the names, secretory, trophic, and anabolic have been applied to these. In the present research, the cat was the animal experimented on, and it was found by the use of small doses of atropine administered successively that all varieties of nerve-fibre were equally and simultaneously paralysed. In other words, the phenomena of atropine poisoning give no indication of the existence of more than one kind of secretory nerve-fibre in the chorda tympani. It is shown that this result is not irreconcilable with the conclusions arrived at by Bayliss and Bradford (*Proc. Roy. Soc.*, 40, 203), with regard to the electrical phenomena which accompany secretion in the submaxillary gland.

W. D. H.

Physiological Action of Borneol. By R. STOCKMAN (*J. Physiol.*, 9, 65—91).—The substances investigated were Borneo camphor, Ngai camphor, and borneol prepared artificially from oil of turpentine. These were contrasted in their action with ordinary or laurel camphor, and with menthol or peppermint camphor.

The three substances first named are identical in chemical composition, and are generally known under the common name of borneol, but they differ considerably in certain physical properties. The

most striking difference is their action on polarised light; an alcoholic solution of Borneo camphor is dextrorotatory, that of Ngai camphor lævorotatory, whilst that of borneol artificially prepared has no action at all on polarised light. The formula of borneol is $C_{10}H_{18}O$, a monatomic alcohol of which common camphor, $C_{10}H_{16}O$, is the aldehyde.

All three varieties of borneol produce the same physiological effects. A very complete investigation was made of their action on the different systems of organs in frogs and in mammals, and complete details of the experiments are given. The following are the general conclusions that are drawn: that laurel camphor, borneol, and menthol form a group of substances very closely allied to each other in physiological action. To these may be added camphor monobromide, $C_{10}H_{15}OBr$, a derivative of laurel camphor, the action of which seems to resemble that of borneol more nearly than that of the other two substances. They are all closely related to the alcohol group in their physiological effects, menthol approaching the latter most nearly, but as the number of hydrogen-atoms diminishes, there is an increased tendency to produce convulsions of cerebral origin. It is in the nervous system indeed that the most marked effects of these drugs are manifested; in mammalia, the symptoms are almost entirely cerebral, the spinal cord being affected much less profoundly; in frogs, on the other hand, the brain is affected first, but subsequently the cord, and lastly the motor nerves are paralysed. Camphor and the essential oils have long been used therapeutically in conditions of increased spinal excitability, and this coincides with the results of pharmacological investigation. As cardiac stimulants, the *modus operandi* of these drugs is again closely related to that of alcohol. Borneol and menthol have, however, a marked effect in dilating peripheral vessels, which ethyl alcohol has not. Pure alcohol is not, however, used therapeutically, but mixed with different ethers in the form of wines and spirits, which dilate the vessels; the resemblance, therefore, between ordinary alcoholic stimulants and the camphor-group of drugs in their action on the circulation is very close.

The Chinese place an exaggerated value on Borneo camphor, its price being about £5 per lb., but whether this is due to a superstitious belief in its virtues, or to any real advantage it has over ordinary camphor is difficult to determine, and can only be decided by long clinical experience. Pharmacological experiments certainly do not show that it is markedly different in its action from the other substances of the same group. It is certainly less irritating locally than laurel camphor, and can be given in much larger doses than the latter without causing untoward cerebral symptoms. W. D. H.

Action of Caffeine and Theine on Voluntary Muscle. By T. L. BRUNTON and J. T. CASH (*J. Physiol.*, 9, 112—136). This paper gives a complete and detailed account of experiments of which a short notice has already appeared (see Abstr., 1887, 985).

W. D. H.

Strychnine Poisoning. By R. W. LOVETT (*J. Physiol.*, 9, 99—111).—There is a marked affinity on the part of certain drugs for

certain organs, or rather a power of certain organs to select some substance from the blood, and by destroying or excreting it, or storing it up, to remove it from the circulation. In the case of strychnine, the question arises, does it exercise its peculiar power on the spinal cord because there is more of the drug present there than in the other organs, or because the cord is more susceptible to its action than muscle, brain, liver, &c.? In attempting to find an answer to this question, the line of work adopted was as follows:—First, by the injection of known amounts of strychnine into frogs of known weight, and by the observation of the time in which convulsions occurred, to construct a table showing the time that various amounts of strychnine require to produce convulsions in frogs of known weight. The table thus constructed may be briefly given thus:—

Dose.	Time between injection of drug and convulsions, in minutes per gram of frog weight.			
	0.657, average of 13 experiments.			
0.0648 mgrm.				
0.0324 "	1.0	"	17	"
0.0216 "	1.5	"	16	"
0.0162 "	2.05	"	8	"
0.013 "	2.54	"	9	"

The second step in the investigation was to take equal weights of the tissues (liver, muscle, spinal cord, blood, &c.) of frogs poisoned by strychnine, to rub each up in a mortar with water, and then to inject the tissue thus finely subdivided, by means of a hypodermic syringe with coarse needle, into a second set of frogs, which were again of known weight. By this means, it was found that injection of the crushed spinal cord rarely failed to produce convulsions, whilst that of the other organs either produced no convulsions at all, or only after a long interval.

Thirdly, by watching the time that convulsions were in appearing, and by knowing the weight of the frogs used, it was possible by consulting the table already given to determine approximately the quantity of strychnine in equal weights of the various tissues of the poisoned frogs. These results are given in tables, but the general conclusion to be drawn from them is that the spinal cord has the power of selecting strychnine from the circulation and of storing it up in its structure. This may be of importance in medico-legal cases, as it shows the best place in which to search for the drug in cases of poisoning where the stomach-contents are not available.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Saccharomyces Apiculatus. By C. AMTHOR (*Zeit. physiol. Chem.*, **12**, 558—564).—*Saccharomyces apiculatus* has been studied by

Rees, Pasteur, Engel, Hansen, and others. It has been found in the juices of the grape and of other ripe fruits, also in beer. Hansen, from his observations on *S. cerevisiæ* and *S. ellipsoideus*, concludes that different varieties of these species exist. This conclusion is supported by the fact that different yeasts perform different kinds of chemical work in the same nutritive solution (see this vol., p. 184). From the present research, a similar conclusion is drawn with regard to *S. apiculatus*. The subject is not studied from the morphological standpoint, but from the point of view of difference in chemical action.

Must from ripe, fresh grapes was sterilised and analysed: it had the following composition:—

Sp. gr. at 15°	1·08234
In 100 c.c. at 15°—	
Extract (Schultze's method).....	21·87
Invert-sugar	20·7216
Acid	1·0125
Fixed acid	1·0083
Volatile acid	0·0033
Nitrogen.....	0·0552
Colour intensity (Stammer's colorimeter).....	4·17

Some of this was divided into two parts; to one part was added a cell of *S. apiculatus* from Niedersaulheim, and to the other, one from Heilbronn. In some weeks' time, when the fermentation had subsided, the two liquids were analysed, with the following results:—

In 100 c.c. at 15°.	Niedersaulheim.	Heilbronn.
Alcohol, vol. per cent.	3·25	4·56
„ wt. „	2·58	3·65
Glycerol	0·31	0·35
Extract (Schultze)	16·09	13·80
Invert-sugar.....	14·23	11·20
Acid	1·06	1·01
Volatile acid (as acetic acid)	0·13	0·11
Ash	0·19	0·19
Phosphoric acid.....	0·03	0·03
Nitrogen	0·04	0·04
Sp. gr.	1·06017	1·05199
Colour intensity	2·5	1·89

The marked differences in the composition of the two wines certainly supports the contention that varieties of the yeast employed exist. If the total acid be taken into account, that is, in the solid residue as well as that in the fluids above mentioned, it is found that the total acid formed during fermentation is about three times greater than that found by Pasteur with ordinary yeast. The volatile acid contains but little acetic acid; it smells like coumaric acid, but was not further investigated.

In beer wort, *S. apiculatus* (Heilbronn), caused in 30 days the formation of only 0.93 per cent. of alcohol. Hansen obtained a similar result, and supposed that this form of yeast never produces more than 1 per cent. of alcohol. Jörgensen, on the other hand, considered that the reason lies in the fact that *S. apiculatus* does not ferment maltose.

Some experiments in the present research support the latter contention. Some of the wort was heated with sulphuric acid to convert the maltose into dextrose; the acid was then neutralised with calcium carbonate, and the liquid evaporated to its original volume, sterilised, and to it was added once more a cell of the *S. apiculatus*. After eight days' fermentation the percentage composition of the liquid was—

Alcohol by volume	2.62
„ by weight	2.11
Acid	0.2625
Volatile acid	0.0618

That is, in a third of the time there was about three times as much alcohol formed as before treatment with sulphuric acid.

The large amount of acidity corresponds with what was observed in wine. If *S. apiculatus* does not ferment maltose, the small quantity of alcohol formed in the first case must have been derived from dextrose. Musculus and Gruber (*Zeit. physiol. Chem.*, 2, 181) show that when diastase acts on starch it produces small quantities of dextrose in addition to dextrin and maltose.

The property of *S. apiculatus* just referred to furnishes us with a means not only of detecting small quantities of dextrose in presence of maltose, but of estimating the quantity present by the amount of alcohol formed.

W. D. H.

Changes occurring in Timothy Grass (*Phleum pratense*).

By E. F. LADD (*Bied. Centr.*, 1888, 574).—Four periods of growth were selected in which to examine the composition of Timothy grass; it was found that the percentage of water diminishes rapidly after blossoming, as does also the woody fibre. As ripening approaches, sugar decreases and starch increases, and the albuminoids are less digestible during the later periods of growth. In the period between blossoming and perfection of the seed, albuminoids are converted into amides, either during the migration of albuminoids from the stem into the seed, or else in conjunction with the migration and conversion of sugar and starch. Consequently, when required for fodder, it is advisable to mow the grass at the period of blossoming.

E. W. P.

Does Grain contain Sugar? By A. v. ASBOTH (*Bied. Centr.*, 1888, 574).—The author contends that the methods employed by Schlösing, König, and others are incorrect, that sugar is not contained in grain, and that in those cases where sugar has been found, it has been produced by the method employed for its detection.

E. W. P.

The Constituents of Acorus Calamus. By H. KUNZ (*Arch. Pharm.* [3], 26, 529—536; compare Abstract, 1886, 895).—Calamin, which was discovered by Thoms, is stated in a more recent publication to be identical with methylamine. Guthzeit has also announced the discovery of methyl alcohol in the aqueous distillate from calamus. Thus we have ethereal oil, acorin, methylamine, and methyl alcohol given as integral constituents of calamus; it still remains to be ascertained which are primary and which secondary constituents. From Thoms' investigation it would appear that the ethereal oil is a decomposition-product of acorin. This author also remarks that the methyl alcohol is derived from the methylamine. During Thoms' separation of calamin, he perceived a distinct, herring-like odour which is characteristic of trimethylamine; this induced the author of the present communication to search for choline in calamus, in which he was successful, as shown by the production of its hydrochloride and the platinochloride, $(C_5H_{13}NO)_2, H_2PtCl_6$. The author further proves the absence of methylamine hydrochloride in the salt residue in which Thoms claimed to have found it, whilst trimethylamine and ammonia were present. J. T.

Constituents of Lupin Seeds. By G. BAUMERT (*Arch. Pharm.* [3], 26, 433—440).—The author gives a summary of the results obtained on this subject during the past 30 years, and appends a list of works and papers published. There are great differences in the composition of seeds of different varieties, thus König gives the mean of 14 analyses of *L. luteus* as: Nitrogenous substances 36·52, fat 4·92, ash 4·04, cellulose 14·04, nitrogen-free extract 27·60; and the mean of 8 analyses of *L. angustifolius* as: Nitrogenous substances 25·37, fat 4·90, ash 3·02, cellulose 12·40, nitrogen-free extract 41·68. It is also known that the various seeds do not all contain the same alkaloids; the constituents of the yellow lupin (*luteus*) seeds are best known. The aqueous extract of lupin seed reacts strongly acid, this being due mainly to the presence of citric acid and a little malic acid, whilst the presence of oxalic acid is somewhat doubtful. The first two acids amount to about 1·92 per cent. of the dry substance. There is less acid in the seeds of the blue lupin (*angustifolius*). Besides the yellow liquid fat extracted by ether, Beyer found a wax-like compound soluble in warm alcohol; both fats contain phosphorus.

The liquid fat contained	C 75·700, H 11·350, P 0·098, O 12·852, Beyer.
The wax-like fat contained	C 72·68, H 10·84, P 1·56, O 14·92, „
Lupin fat	C 75·94, H 11·59, — O 12·47, König.

With concentrated sulphuric acid, the powdered seed gives a red coloration due to a cholesterin, which, according to Schulze and Barbieri, has the same crystalline form as ordinary cholesterin, but melts at 136° to 137° instead of at 145°; its specific rotatory power is $[\alpha]_D = -36·4$. Of carbohydrates neither starch nor inulin occurs according to Ludwig, and sugar is only found as a decomposition product; a dextrin-like substance with dextrorotatory power has been described;

this by the action of mineral acids produced a sugar capable of reducing Fehling's solution. Steiger has found this to be a white hygroscopic powder of the composition $C_6H_{10}O_5$, easily soluble in water, almost insoluble in alcohol and ether. Its aqueous solution is not coloured by iodine, diastase has no action on it, nitric acid converts it into mucic acid, and by treatment with acetic anhydride it takes up three acetyl-groups. The product, therefore, is not glucose but is identical with galactose from milk-sugar, hence the carbohydrate from *L. luteus* is named galactan, and considered as the β -compound to distinguish it from α -galactan, Muntz's galactin obtained from lucerne. Schulze and Steiger obtained another compound from the same variety also insoluble in water, and convertible into galactose by the action of boiling acids. This so-called paragalactin has the formula $C_6H_{10}O_5$, and yields a triacetyl-compound which decomposes at 225° without melting, whilst that from β -galactan melts at $101-102^\circ$. Besides the above carbohydrates, cellulose to the extent of 12 to 14 per cent. occurs in lupin seeds. The albumin of these seeds consists mainly of conglutin according to Ritthausen, along with small quantities of legumin and a little vegetable albumin. Conglutin and legumin differ in their solubility in salt solution; the former contains 18.67 per cent. nitrogen, and the latter 17.41. All lupins probably contain several alkaloids, amounting to 0.04 to 0.81 per cent. The author has found in yellow lupin the crystallisable alkaloid lupinine, $C_{21}H_{40}N_2O_2$, and the liquid lupinidine, $C_8H_{15}N$. In the blue lupin only a liquid alkaloid has been investigated which Hagen has named lupanine; its composition is $C_{15}H_{25}N_2O$. Campani has obtained yet another alkaloid from the seeds of *L. albus*.

Other nitrogen compounds of the amide-group have not been isolated from the ungerminated seed; but after germination a series of compounds produced by the decomposition of the albumin has been obtained by Schulze, Barbieri, and Steiger: asparagine is the principal product, and there are besides phenylamidopropionic acid, amidovaleric acid, leucine, tyrosine, xanthine, hypoxanthine, lecithin, peptone, and arginine, $C_6H_{14}N_4O_2$, a base analogous to creatinine. Choline also was detected.

Schulze and Barbieri found a new glycoside in *L. luteus* of the composition $C_{26}H_{32}O_{16}$ which they named lupinin, but it is better called lupiniin to distinguish it from the similarly named alkaloid. It crystallises in fine needles, dissolves in alkaline solutions with a yellow colour, and on treatment with acids takes up 2 mols. H_2O with the formation of lupigenin, $C_{17}H_{12}O_8$, and glucose. Hot water also produces the reaction.

J. T.

Influence of a Crop or Covering on the Physical Characters of a Soil. By E. WOLLNY (*Bied. Centr.*, 1888, 505—524).—In continuation of his previous experiments (*Abstr.*, 1884, 922), the author has investigated the effect on the amount of water when the soil is bare or covered with vegetation, &c. He finds that soil covered by vegetation is drier than if it were bare and unshaded, whilst if it be covered by straw, farmyard manure, &c., it is moister during warm

weather than if it were bare, the moisture present is higher the thicker the covering, and it is driest when there is a covering of live vegetation. It is consequently an error to suppose that land is kept moist by being shaded by a crop of potatoes, peas, &c., the contrary being the case, and is occasioned by the shelter which the plants afford to the soil, the rain remaining on their leaves and there evaporating, further, the dry condition is assisted by the transpiration of water by the leaves themselves. The dry condition of the surface is also dependent on the activity of growth of the plants and their close standing; but when the surface is covered by any dead matter, then the state of affairs is reversed, and the soil is the moister the thicker the covering; the amount of water in a bare uncovered soil is a mean of the other two quantities. As regards the amount of drainage water, it is found that a greater quantity passes into the deeper strata when the soil is bare than when it is covered, and a greater quantity percolates through a soil covered by straw, &c., than through a perfectly bare soil. The character of the plants growing also affects the amount of drainage, unmanured allowing of more drainage than manured plants, and when vegetation is thick and strong there is but little drainage; the covering of dead material only increases the drainage so long as it is not more than about 5 cm. thick, beyond that drainage is diminished. Full accounts of the experiments made and tables of results are given.

E. W. P.

Manuring of Clover. By J. SAMEK (*Bied. Centr.*, 1888, 527—529).—On sandy loam, clover was grown and manured with various manures, including basic slag. The least effect on the first cut was produced by the slag, whilst the third cut was heavier than that produced by any of the other manures. Gypsum had no effect. The increase produced by potash salts was neutralised by the extra expense incurred. Of nitrogenous manures, blood-meal mixed with superphosphate was found to be the best.

E. W. P.

Manuring with Nitre. By M. FLEISCHER (*Bied. Centr.*, 1885, 525—527).—White lupines, clover, potatoes, &c., were manured with a mixture of kainite, superphosphate and Chili saltpetre, the latter in increasing quantities. An increased yield of the leguminous plants was obtained, and the increase more than paid for the extra expenses. The land was light.

E. W. P.

Basic Slag as a Manure for Oats. By A. EMMERLING (*Bied. Centr.*, 1888, 529—531).—In the dry season of 1887, and on a loamy soil, excellent results were obtained from a mixture of basic slag and Chili saltpetre in the proportion of 8 : 3. The superiority of basic slag over superphosphate is accounted for in this year, by the action of superphosphate not being brought out fully unless there is a fair supply of moisture.

E. W. P.

Fossil Milk. By V. STORCH (*Bied. Centr.*, 1888, 566—567).—This so-called fossil milk, which occurs as a white, porous mass in Bergthorshvol in Iceland, contains more phosphoric acid than is found in

coprolites, &c., the proportion of lime and phosphoric acid present closely resembling that found in the coagulum of milk in use in Iceland, and called "Skyr," which is produced by the combined action of rennet and sour milk. Organic matter has been detected, which reacts with tungstic acid, tannin, and iodine, but which produces no results with Millon's reagent and does not give the biuret reaction. The best sample contained 11 to 12 per cent. combustible matter, whilst the pure organic matter contained 10 per cent. of nitrogen. Under the microscope, a tissue consisting of pyrenomycetes was observed.

E. W. P.

Analytical Chemistry.

Testing Potassium Carbonate. By E. BOHLIG (*Arch. Pharm.* [3], 26, 541—542).—To avoid error in testing potassium carbonate by means of silver nitrate solution, the author recommends the following method of procedure:—

Pour gradually a solution of 0.5 gram of potassium carbonate into a solution of 3 grams of silver nitrate in 100 c.c. of distilled water. The precipitate should be pure white, not yellowish. A further test may be made by dropping silver nitrate solution not in excess into the carbonate solution. If the precipitate is now white, the carbonate also contains hydrogen carbonate. J. T.

Action of Iodine on Hydrogen Arsenide and Antimonide. By O. BRUNN (*Ber.*, 21, 2546—2549).—Hydrogen arsenide present in hydrogen sulphide can be determined by passing the mixture through a tube containing iodine. The contents of the tube are afterwards washed into a glass, hydrogen sulphide free from hydrogen arsenide passed through, and the arsenic sulphide so formed is determined as ammonium magnesium arsenate, which is dried at 102—103° and weighed. Some results obtained by the method are given, as well as results obtained with the same mixture of gases, by passing the gas through a dilute solution of silver nitrate, and determining the arsenious acid by means of an iodine solution. The results show that the method is trustworthy. Hydrogen antimonide, which behaves towards iodine similarly to the arsenide, can also be readily determined by this method. N. H. M.

Detection of Poisoning by Caustic Alkalis. By VITALI (*Arch. Pharm.* [3], 26, 516; from *L'Orosi*, 1888, 37).—Detection is difficult, as the alkali quickly becomes converted into carbonate or it combines with albuminoid substances. If solid matter such as flesh is to be examined, it is finely divided and digested for 24 hours with 8 volumes of alcohol, whilst liquids are evaporated to dryness at the lowest possible temperature, and with a minimum amount of ex-

posure to the air. A little of the alcoholic extract is shaken with mercurous chloride, which blackens in presence of caustic alkalis whether free or combined with proteid substances. The black powder should disappear on digestion with nitric acid, otherwise it may be due to sulphur compounds. If a positive result has been obtained, the remainder of the alcoholic solution is treated with sulphuric acid when the alkaline sulphate is precipitated. The precipitate is dried and ignited, dissolved in a little water, and a portion is used to obtain crystals by evaporation, whilst the remainder is employed to determine whether sodium or potassium is in question. This gives only the free alkali: to obtain the alkali combined with albuminoid compound, the residue from the original alcoholic extract is extracted with boiling water, to this solution, after being brought to a syrup, is added 6 volumes of absolute alcohol, and then sufficient ether to precipitate all that will come down. If the precipitate blackens mercurous chloride, caustic alkali combined with albuminoid matter is indicated. The nature of the alkali is determined by igniting the precipitate, dissolving in hydrochloric acid and examining further. Finally, the alkali in combination with proteid substances insoluble in water is obtained by extracting the flesh residue insoluble in alcohol and water with dilute hydrochloric acid and proceeding as above.

J. T.

Haycraft's Method of Estimating Uric Acid in Urine. By A. HERRMANN (*Zeit. physiol. Chem.*, **12**, 496—501).—Some modifications in the details of Haycraft's method of estimating uric acid in urine (*Brit. Med. Jour.*, **2**, 1885, 1100) are suggested, and its accuracy tested in comparison with Ludwig's method (*Wiener Med. Jahrbücher*, 1884). It was found that on the average, the results by Haycraft's method were 0.0029 gram per 100 c.c. of urine (or 7.9 per cent. of the total uric acid) higher than by Ludwig's method. With solutions of pure uric acid, there is by both methods a loss of 2 per cent., and the explanation of the difference probably is, that the ammoniacal silver solution used by Haycraft precipitates other substances from the urine; for instance, those of the xanthin-group in addition to uric acid.

The occurrence of sugar or albumin in the urine does not at all influence the reactions on which Haycraft's method depends. This is one great advantage of the method; another is the ease and rapidity with which the analysis can be made, and for a series of comparative clinical observations it is a very suitable method indeed.

It is pointed out that the addition of sodium hydrogen carbonate to the urine does not entirely prevent the reduction of the silver as stated by Haycraft; but that the reduction is so small in the time occupied by the analysis, especially if the filter-pump is used, that it may be disregarded.

W. D. H.

Estimation of Uric Acid in Urine. By F. CZAPEK (*Zeit. physiol. Chem.*, **12**, 502—511).—This method claims to be even simpler than Haycraft's, of which it is a modification (see preceding Abstract), as it does away with the use of the filter-pump. It, however, like Haycraft's, gives too high results when tested with urine, and the delicacy of the two tests is about equal.

With pure uric acid in solution, it is stated to give results equally as good as those obtained by Ludwig's method by direct estimation. This method is recommended for use in clinical work. The essential feature is that a known quantity of ammoniacal silver solution is added to the urine, the uric acid being thus precipitated as silver urate; this is filtered off, and the silver is estimated not in the precipitate (as in Haycraft's method), but in a certain measured proportion of the filtrate. From these data, the amount of silver residue is obtained, and thus the amount of silver and uric acid in the precipitate. By this process not only is the use of the filter-pump unnecessary, but it also does away with the washing of the precipitated urate which is very troublesome. The silver in the filtrate is estimated by warming and titrating with potassium sulphide or sodium sulphide solution, the browning of lead paper being the indicator used for ascertaining the termination of the reaction. Several successive titrations are necessary to obtain a correct result. W. D. H.

Densimetric Estimation of Proteïds. By HUPPERT and ZÁHOŘ (Zeit. physiol. Chem., 12, 467—483).—Methods have been devised for the quantitative estimation of proteïds in solution by means of multiplying the loss in specific gravity which such solutions undergo on the removal of the proteïd, by a constant factor, under the mistaken impression that the loss of density is directly proportional to the amount of proteïd removed. In the case of grape-sugar where a similar method has been adopted, Budde (this vol., p. 198) has shown that from its very nature the factor is a variable one; and the first part of the present paper is devoted to an algebraical demonstration that the same is the case with albumin in solution. For the complete exposition of this point, the original paper must be consulted. The essential facts are, however, these: the sp. gr. of a liquid is its weight divided by its volume; and its volume may be obtained by dividing its weight by its sp. gr. Let x = grams of proteïd in 100 grams of solution:

$$\begin{aligned} \text{Let } v &= \text{sp. gr. of the solution,} \\ v_2 &= \text{,, of the proteïd,} \\ v_1 &= \text{,, of solution minus proteïd.} \end{aligned}$$

The value of v_1 may be calculated; it is the weight of the proteïd-free liquid divided by its volume, which is the volume of the original liquid, $\frac{100}{v}$ minus the volume of the proteïd removed $\frac{x}{v_2}$: therefore

$$v_1 = \frac{100 - x}{\frac{100}{v} - \frac{x}{v_2}};$$

this gives as the value of x —

$$x = \frac{100 v_2}{v(v_2 - v_1)} (v - v_1),$$

$v - v_1$ is the loss of sp. gr., and the fraction $\frac{100 v_2}{v(v_2 - v_1)}$ is the sup-

posed constant factor: that it cannot be constant is seen from the fact that v and v_1 are both variable quantities. Experiment also showed that v_2 , the sp. gr. of the contained proteid, is likewise variable. If x , the percentage of proteid, is known, v_2 can be calculated from the same formula as follows:—

$$v_2 = \frac{xvv_1}{xv - 100(v - v_1)}.$$

A series of 20 estimations of the amount of proteid coagulable by boiling after adding acid was made. The value x was determined by weighing the proteid precipitate and the specific gravities by Sprengel's pycnometer. The solutions employed were ascitic fluids, blood plasma, and solution of white of egg, and the value v_2 (sp. gr. of the proteid) was found to vary between 1.352 and 1.405. The average of the 20 observations gives $v_2 = 1.3747$ which may be used in approximate determinations. In connection with the value of v_2 (sp. gr. of the proteid), it may be noted that it is influenced by the quantity of proteid and the density of the solvent, v_1 . Now it is known that certain salts precipitate proteids in an unchanged state when the concentration of the salt solution reaches a certain height, salt solutions of small density do not precipitate the proteid, but they increase its density; when the concentration of the salt in solution is increased, a point is at last reached where the contraction of the proteid becomes so great that it is precipitated. The concentration of the salt solution will also vary with the salt used.

Tables are then given of comparative experiments in which the quantity of proteid was determined by weighing, and by calculation from such formulæ as have been instanced; and it is shown that the densimetric method yields only approximate results. W. D. H.

Densimetric Estimation of Albumin in Urine. By H. ZÁHOŘ (*Zeit. physiol. Chem.*, 12, 484—495).—Although it has been shown (see preceding Abstract) that from the theoretical side there is much to be urged against the densimetric method, yet it is found in practice, in cases where accuracy to the first place of decimals is sufficient, that the method is extremely quick and handy. This is felt nowhere so much as in estimations of albumin in urine, and the following method is simple, and can be carried out clinically:—

The filtered urine is mixed with just so much dilute acetic acid that when it is boiled all the albumin is coagulated; the right proportion may be ascertained with a small quantity of the urine in a test-tube beforehand. On being filtered from the coagulum, the filtrate should give no cloudiness with acetic acid and potassium ferrocyanide. A quantity of the urine is then placed in a flask firmly closed with a clean caoutchouc stopper. The flask is hung for 10 to 15 minutes in a large bath, filled with water kept boiling. By this means the albumin is precipitated. It is then filtered off, the funnel leading through a cork with a hole in it into a flask, and being covered with a glass plate. The density of the urine and the filtrate is then estimated, not with a pycnometer (that is unnecessary for clinical work), but with an aræometer marked to four places of decimals. Both fluids

must be kept at the same temperature. This is best done by placing them in two cylinders, both immersed in a large vessel of water, which should be kept at the same temperature if a series of observations are to be made. The temperature of 17.5° will be found most convenient. The difference between the two specific gravities is then multiplied by 400, and the product gives the number of grams of albumin in 100 c.c. of urine.

A large number of illustrative experiments are quoted, in which the approximate accuracy of this simple process is demonstrated. The number 400 is the mean in round numbers of the factor

$\frac{100v_2}{v(v_2 - v_1)}$. The question naturally arises why a constant factor should give such good results in albuminous urine, when not only theoretically but also in practice it yields fallacious results in other albuminous fluids, such as the blood, transudations, white of egg, &c. The reason is that the factor must be multiplied by the difference in the specific gravities. In proteid solutions (other than albuminous urine) this difference varies from 0.0016 and 0.0128, whilst in albuminous urine this difference is much smaller, varying between 0.00012 and 0.0020, that is, in the former case the difference is from six to 13 times greater than in the latter, and therefore so many times greater will be the error introduced by the use of a constant factor. In the case of urine, this error may be neglected. W. D. H.

Biological Test for Malt. By F. FAULKNER and W. VIRTUE (*Bied. Centr.*, 1888, 481—482).—A flask of 100 c.c. capacity is half filled with distilled water, closed with cotton-wool and sterilised; after cooling to the proper temperature for mashing, a teaspoonful of malt is introduced, and the whole is kept for two hours at the mashing temperature on a water-bath, after which it is cooled and placed in a thermostat. After some hours, the upper liquid becomes clear; observations must now be made as to whether the liquid becomes thick, or if gas is evolved, both of which occurrences are signs of decomposition. This process serves to estimate the quality of malt. Comparative experiments must necessarily be made under like conditions; the higher the temperature in the thermostat (with certain limits) the more rapid will be the development of micro-organisms; a concentrated wort decomposes less rapidly than a dilute: if much acid is present, then the wort more readily resists change, consequently the acidity should be reduced before testing; the presence of caramelised matter tends to preserve wort unaltered, so that a dark malt must be carefully examined for caramel. The presence of coombs may retard or advance decomposition, as there is more or less of caramelised compounds present. E. W. P.

General and Physical Chemistry.

Chromium and Manganese in Fluorescent Mixtures. By L. DE BOISBAUDRAN (*Compt. rend.*, 107, 311—314).—Calcium carbonate containing chromium oxide, precipitated by ammonia, becomes green when calcined in presence of air, but if it contains a trace of sodium carbonate it becomes yellow. A similar mixture precipitated by sodium carbonate becomes green, however, when strongly heated, if it is previously moistened with hydrochloric acid or ammonium chloride. In a vacuum, the yellow substance shows a green fluorescence, but remains yellow if the discharge is not too intense and its passage is not long continued. If, however, the tube is very gently heated whilst the discharge is passing, the substance becomes green, the change taking place more quickly the smaller the quantity of sodium present. After cooling, the substance shows a green fluorescence.

When the yellow mixture is exposed to the air for some time, it is converted into carbonate without change of colour, but is no longer fluorescent. When gently heated in a vacuum, the colour changes to green, but the mixture remains non-fluorescent. If, however, it is strongly heated in presence of air, it regains its fluorescent properties. A similar mixture containing 5 per cent. of chromium oxide becomes green when heated in a vacuum, and remains green if kept for several months in an open vessel, but then will not fluoresce.

The fluorescence of calcium oxide containing iron or chromium cannot be attributed to the simultaneous presence of small quantities of copper. It would seem, therefore, that both ferric oxide and chromic oxide are active substances with respect to calcium oxide, but their activity is of an order somewhat different from that of other substances. The green in the spectrum of the fluorescence of calcium oxide containing iron or chromium is usually less intense than with calcium oxide alone, but the difference is not sufficient to decide whether the activity of iron and chromium is positive or negative. Whilst, however, they have little effect on the green, they are negatively active to the other rays, the intensity of which is reduced, and hence the colour of the fluorescence becomes green. C. H. B.

Influence of Inactive Substances on the Specific Rotatory Power of Tartaric Acid. By R. PRIBRAM (*Monatsh.*, 9, 485—504).—The author confirms the experiments of Landolt (*Abstr.*, 1881, 257), and finds that the specific rotatory power of tartaric acid rapidly diminishes when acetone is added to the aqueous solution. Alcohols behave in a precisely similar manner, those of highest molecular weight producing the greatest change. Solutions originally dextro-rotatory may be made laevorotatory by the addition of butyl alcohol; whilst isomeric alcohols, propyl and isopropyl on the one hand, and trimethyl carbinol and isobutyl alcohol on the other, bring about

practically similar changes. Acetic acid also lowers the rotatory power to such an extent as to make it possible to estimate the amount of it present in aqueous solutions by means of tartaric acid.

G. T. M.

Transparency of Metals. By W. WIEN (*Ann. Phys. Chem.* [2], **35**, 48—62).—This research was undertaken with a view of investigating more fully than had hitherto been done, the relation between electrical conductivity and optical transparency in metals, with the object of determining how far they agree with Maxwell's law.

Maxwell's experiments with gold leaf had given a greater transparency relatively to its electrical conductivity than was consistent with the law referred to, but he considered the results open to some doubt owing to defects in the method of observation.

The metals experimented on by the present author were platinum, gold, silver, and iron.

The intensity of the beam of light, both with and without a thin layer of metal interposed, was determined by measuring the change of resistance in a modified form of bolometer forming one of the arms of a Wheatstone bridge. The bolometer was formed of silver foil covered with lampblack to reduce the reflection to a minimum, and was found to be very sensitive, as the temperature coefficient of silver is a high one, and a sufficiently large piece of the thin foil could be employed to intercept all the rays from the source of light, without making the resistance too small for its variations to be determined with accuracy.

The author finds, in the case of the metals experimented with, that the absorption is less, and therefore the transparency greater than is in accordance with Maxwell's law.

Similar results were obtained for the dark rays of the spectrum, showing that there was no better agreement with Maxwell's law in the case of the longer waves, although according to Maxwell's theory, there ought to be a closer agreement in the latter case, as his theoretical law would only be strictly true for waves of infinite length.

G. W. T.

Voltaic Balance. By G. GORE (*Chem. News*, **58**, 64).—Two couples of zinc or magnesium and platinum are immersed simultaneously in two vessels of distilled water, they are then opposed to each other through an ordinary astatic galvanometer of 100 ohms, or through a Thomson's reflecting galvanometer of 3040 ohms resistance, so as to balance one another and cause no deflection; this arrangement is remarkably sensitive in some cases. For example: with a zinc and platinum couple and the astatic galvanometer, 1 of iodine in about 3,520,970 parts of water, or 1 of hydrochloric acid in about 9,388,185, or 1 of chlorine in about 1,300,000,000, causes deflection, whilst with the reflecting galvanometer 1 of hydrochloric acid in about 23,250,000 of water may be detected; on the other hand, with a magnesium and platinum couple, 1 of bromine in about 344,444,444 of water, or 1 of chlorine in about 17,612,000,000, and with the reflecting galvanometer even more dilute solutions upset the equilibrium.

Large quantities of neutral salts are required to disturb the balance.

The degree of sensitiveness varies directly with the affinity, the dissolved substance has for the positive metal, and indirectly with its affinity for the negative metal. D. A. L.

Electrification of a Gas by a Glowing Platinum Wire. By R. NAHRWOLD (*Ann. Phys. Chem.* [2], **35**, 107—121).—In his former investigations (*ibid.*, **5**, 460, and **31**, 448), the author found that a glowing platinum wire immersed in atmospheric air gives rise to an electrification in the surrounding air, even when the wire itself is not electrified by any external source. He also found that when the wire glows feebly, the electrification is positive, but becomes negative when all dust particles are consumed and the wire is glowing brightly. He came to the conclusion that these results were to be accounted for by the burning of dust particles and other non-gaseous matter in the vicinity of the wire, and by the disintegration of the wire at higher temperatures, and the consequent giving off of charged particles of metal. These conclusions are in conformity with the results obtained in the present paper, which likewise confirm the results of Elster and Geitel (*Ann. Phys. Chem.* [2], **31**, 109), that a feebly glowing platinum wire immersed in atmospheric air becomes negatively charged, but charges the air positively.

When the air was replaced by hydrogen, similar results were obtained when the gas contained dust particles, or when the wire was not perfectly clean, but at higher temperatures, although a negative charge was obtained, it was much less than with atmospheric air, and at the same time it was definitely proved that the disintegration of the wire is very small in hydrogen compared with its amount in atmospheric air. A curious result was observed when the wire, after exposure to the air, was heated in an atmosphere of hydrogen, namely, it was destroyed when a dull red heat was attained. This did not occur when the wire was left in the hydrogen for some time before heating it, and the author attributes the result to the formation of oxyhydrogen gas in the pores of the platinum, and its explosion when the wire is heated. He considers that the results of the investigation afford further support to his former conclusion that gases are incapable of being statically charged with electricity. G. W. T.

Conductivity of Fused Mixtures of Sodium and Potassium Nitrates. By E. BOUTY and L. POINCARÉ (*Compt. rend.*, **107**, 332—334).—The electric conductivity of fused mixtures of the two salts in widely varying proportions at temperatures between 306.7° and 346.6° agrees closely with that calculated from the known resistances of the constituents. In no case does the difference between the observed and calculated value exceed 0.3 per cent. C. H. B.

Present Condition of the Theory of the Electrolysis of Solutions. By F. KOHLRAUSCH (*Elektrotechnische Zeitschrift*, **8**, 258—265).—This paper contains a valuable summary of the results of researches in electrolysis from the discovery of the electrolysis of water by Nicholson and Carlisle (*Gilbert's Ann.*, **16**, 340) in 1800 down to the present time.

The hypothesis of Grothuss (*Gehlen's Journal*, 8), propounded eight years later, that electrolytic compounds consist of molecules with opposite electrifications of their own, and that during electrolysis they are separated and travel in opposite directions through the liquid, still forms the essential basis of all inquiries. This was first expressed quantitatively by Faraday (*Exp. Res.*, 7th Ser.) in the statement that the quantity of any constituent separated will be proportional to the quantity of electricity which has traversed the electrolyte, and to the chemical equivalent of the constituent, but will be independent of the compound from which the constituent is taken. This statement, however, is not strictly true of the more complex compounds.

Faraday's law may, from his own researches, together with those of Soret, Buff, Rayleigh, Shaw, and others, be accepted as an exact one with the exception mentioned above; and it follows that each of the constituents into which a molecule is broken up must retain a constant positive or negative charge throughout its electrolytic movements.

About 20 years after the statement of Faraday's law, Hittorff (*Ann. Phys. Chem.*, 89, 177; 98, 1; 103, 1; 106, 337) showed that while the constituents into which each molecule is divided do travel in opposite directions, they travel with unequal velocities.

The results of Hittorff's researches point to the conclusion that the water of the solution plays no part in the decomposition, and that no appreciable part of the conductivity is due to it. This is only a special case of the more general experimental fact that, with the exception of metals, almost all liquids which are good conductors consist of mixtures of two or more chemical compounds (F. Kohlrausch, *Ann. Phys. Chem.*, 15, 271).

The author points out that the investigations of Buff, Poggendorff, Hittorff, von Helmholtz, and others have made it quite impossible to assume that electrolytes conduct like metals, and that electrolysis is a mere secondary effect. This conclusion is in agreement with the fact that electrolytic conductivity is quite independent of transparency to light and radiant heat (F. Kohlrausch, *Ann. Phys. Chim.* [2], 6, 29; S. Bidwell, *B.A. Report*, 1886, 309).

In spite of this, however, it is found that electrolytes obey Ohm's law, even with such small E.M.F.s. as the millionth of a volt acting through a thickness of a centimetre of liquid, and no effects due to inertia have been observed, even with rapidly alternating currents or currents of short duration (Kohlrausch and Hippoldt, *Ann. Phys. Chem.*, 138, 370; Cohn, *ibid.* [2], 21, 667).

The author gives a series of interesting curves representing the conductivity of various substances in solution, the molecular strength of the solution being taken as abscissa, and the corresponding conductivity as ordinate. The curves are all found to be of the same general character, rising more or less rapidly to a maximum as the strength increases, and then diminishing again. The curves show very clearly that similarity of chemical constitution carries with it a similarity in the march of the conductivity. This similarity in the curves is no longer observed if the strengths of the solutions are

given in terms of the percentage composition instead of in terms of the chemical equivalents, which gives an additional proof of the fact that the chemical equivalent is the natural unit of measurement in electrolytic phenomena.

With regard to the influence of temperature, it is found that substances which behave in nearly the same way at any given temperature undergo similar changes in conductivity when the temperature varies. The conductivities of different solutions are found to tend towards equality as the temperature increases (F. Kohlrausch, *Ann. Phys. Chem.* [2], **6**, 191 and 196).

In the case of sulphuric acid, the curve, after reaching a maximum when the solution contains about 30 per cent. of sulphuric acid, falls to a minimum when the proportions of acid and water are such as to form the crystallisable compound $\text{H}_2\text{O} + \text{H}_2\text{SO}_4$, confirming the conclusion that the conductivity is less for a chemical compound than for a mixture. It then reaches a second maximum and falls to a minimum again when the solution consists of pure sulphuric acid. If the anhydrous acid is now added the conductivity again increases slightly, and ultimately falls almost to zero. It is instructive to note that the conductivity of the pure sulphuric acid is much less than that of the less stable compound $\text{H}_2\text{O} + \text{H}_2\text{SO}_4$.

The curve for sulphuric acid does not coincide with those for nitric and hydrochloric acids, which confirms the theory that the former is a bibasic while the latter are monobasic acids. When, however, the solutions are extremely dilute, the curves agree much more closely, from which it would appear that sulphuric acid when very largely diluted with water tends towards the constitution of a monobasic acid.

There is found to be a distinct connection between the mechanical viscosity of solutions and their conductivities, a series of salts arranged in order of conductivity agreeing in general with the series arranged in order of fluidity. The maximum value of the conductivity also is usually attained the sooner, the greater the viscosity.

A number of instances are known in which substances continue to conduct electrolytically, even when they become solid, and it is found that very little effect is produced on the conductivity of a solution by solidifying it by the addition of gelatin. This, however, is not in any contradiction with the relations between viscosity and conductivity, for viscosity and mechanical rigidity are by no means identical, and, moreover, gelatinous bodies are not homogeneous.

In the case of solutions of electrolytes with monobasic acids, it is found that every constituent has a certain definite speed of its own, whatever be the compound in which it occurs. The author gives the following table of ionic speeds for a molecular concentration 0.1:—

K.	NH_4 .	Na.	Li.	Ag.	H.	Ba.	Mg.	Zn.
+ 51	50	33	25	42	272	31	25	24
Cl.	I.	NO_3 .	ClO_3 .	$\text{C}_2\text{H}_3\text{O}_2$.	OH.			
— 54	54	48	43	27	146			

The sum of the speeds of the two constituents of a salt will give its molecular conductivity, that is, the ratio of the conductivity to the

number of electrolytic molecules in unit volume of the solution. The numbers thus obtained in various cases are found to be in close agreement with those determined by direct experiment. As examples of the absolute velocities of the ions, that of hydrogen is found to be in millimetre-seconds 0.3, of potassium or chlorine 0.06, of lithium 0.028 for a slope of potential of 1 volt, and a molecular concentration of 0.1. They would of course be greater in more dilute solutions.

These numbers, of course, are only the mean values of the components of the velocity in the direction of the current, for the electrolytic movements cannot be regarded as being of such a nature that all the constituents should have identical velocities at any given moment.

In connection with the fact that electrolysis depends on differences in the motion of the constituent molecules, it is interesting to note that electrolytes which are good conductors generally diffuse rapidly in water, and the converse also holds, from which it follows that those substances which allow great freedom of motion to the constituent molecules, are in general those in which the entire molecules move most freely. Since electrolytes obey Ohm's law, and since also decomposition begins with any E.M.F., however small, we cannot assume that the molecules are broken up by the E.M.F. Clausius, therefore, assumed (*Ann. Phys. Chem.*, **101**, 358) that in an electrolyte a certain number of the molecules are dissociated, possibly by the action of the water, and that these free molecules are the first which are acted on by the electrical forces, the decomposition then extending by interchanges to the others.

If it is also assumed that the chemical action of an acid or other substance starts, not from the molecules in combination, but from the dissociated molecules, then Clausius's theory gives a simple explanation of the observed relation between conductivity and rapidity of chemical action.

The original paper contains a large number of references to original memoirs, of which a few only are given above. For the others reference must be made to the original paper, or to a translation in *The Electrician*, **21**, 466—467 and 504—507. G. W. T.

Electrolysis with Alternating Currents. By E. DRECHSEL (*J. pr. Chem.* [2], **38**, 75—77).—The author complains that Manœuvrier and Chappuis (this vol., p. 1005) have not acknowledged his work on this subject. The spontaneous detonations which occur when water is electrolysed by alternating currents are not due to the incandescence of the electrodes, nor need the latter come in contact with a vessel of the mixed gases, the detonations occurring even when the electrodes are fully immersed in the liquid; the author attributes them to sparking. A. G. B.

Production of Ozone by the Electric Discharge. By BICHAT and GUNTZ (*Compt. rend.*, **107**, 334—336).—The ozoniser employed consisted of a platinum wire, 0.1 mm. in diameter, stretched along the axis of a cylinder of the same metal through which passed a slow

current of oxygen at constant pressure. The wire was connected with a Holtz machine and an absolute electrometer, and the cylinder was connected with the earth and a galvanometer. By means of a Mascart's "Trop-plein" a constant discharge was obtained.

For the same intensity of discharge, the negative effluve produces 10 times as much ozone as the positive effluve. If the discharge takes place between a platinum point and a disc of the same metal, the difference is less marked, but is still very distinct. This result is explained if it is assumed that the production of ozone is not a result of electrification, but of a rise of temperature, since the negative discharge is hotter than the positive.

For the same velocity of gaseous current, the quantity of ozone produced increases with the intensity of the discharge and the difference of potential, but there is no simple quantitative relation. At first the quantity of ozone formed varies as the square of the potential; but this only holds good for potentials up to 20 C.G.S. Faraday's law does not apply.

In the ozone apparatus devised by Berthelot, it is seen when the discharge takes place in the dark that the oxygen is illuminated by an infinite number of minute sparks commonly termed a "rain of fire," this being more brilliant the lower the resistance. The quantity of ozone also varies with the resistance, and is lower the less brilliant, or, in other words, the cooler, the discharge. In the same apparatus a discharge which produces no sparks produces no ozone. It is evident from these observations that the formation of ozone cannot be due to a dielectric polarisation or to a state of strain resulting from it. In Berthelot's apparatus, the quantity of ozone formed has no relation to the difference of potential between the armatures. The capacity is constant, and therefore Faraday's law is applicable.

The production of ozone is due to a more or less considerable elevation of the temperature of the oxygen resulting from the passage of the electric discharge. The oxygen, in fact, is under conditions similar to those in a Deville's hot-and-cold tube.

With an ozoniser consisting of a metallic point and disc, only 0.4 per cent. of the energy of the discharge is utilised in the production of ozone. With Berthelot's apparatus, on the other hand, as much as 89 per cent. of the energy may be utilised. C. H. B.

Electrical Dialysis. By H. N. WARREN (*Chem. News*, 58, 76).—The author has devised an arrangement for the purpose of converting a substance "into an allied form" by the aid of electrolytical nascent hydrogen, and at the same time of dialysing the product. A tube closed at the bottom by a parchment diaphragm serves as the dialyser, and is fitted with a cork carrying a tube with some mercury in it, and connected to a pendant platinum plate by a wire of the same metal, fused through the lower end. This dialyser contains the substance to be acted on, and is suspended in an outer vessel, containing—1, an aqueous solution of the reagent which is to combine with the substance; 2, a porous pot, in which is placed some solid ammonium chloride, a zinc rod, and some water. The liquids in all three vessels are adjusted to the same level, the platinum plate in

the dialyser is made the negative electrode, and the zinc rod the positive pole of a galvanic circuit. With copper sulphate and sodium chloride in the dialyser, and dilute sulphuric acid in the outer vessel, copper is deposited on the platinum and sodium sulphate dialyses. Potassium dichromate gives rise to a deposit of chromic hydroxide and a dialysate of potassium sulphate. With ricinoleic acid in the dialyser and sodium carbonate outside, sodium stearate forms. Many other substances have been treated.

D. A. L.

The Specific Heats of some Metals from the Ordinary Temperature up to 300°. By A. NACCARI (*Gazzetta*, 18, 13—31). The author criticises the methods employed by those physicists who have made determinations of the specific heats of metals at high temperatures, and points out the various sources of error in them, condemning especially the methods of Bède and Byström, whose results he considers to be of very little value.

In the apparatus employed by the author, the metal, whose specific heat had to be determined, was heated in a metal basket suspended in an air-bath with double walls, the temperature of which was kept constant by passing the vapour of a liquid through the annular space between these walls. It was so arranged that the metal and the basket could be dropped direct from the air-bath into the calorimeter; this latter was made of brass, and fitted with a stirring apparatus and a delicate thermometer graduated to $\frac{1}{10}$ th of a degree. The thermometers employed were carefully compared with the air thermometer, and the 100° point verified from time to time; further, by choosing the thermometer whose scale was best adapted for the temperature in the calorimeter during any given experiment, the correction for the column of mercury not immersed in the liquid could be reduced to a minimum. One of the chief causes of error in methods formerly employed was the use of water as the liquid for the calorimeter; when a metal at a high temperature is plunged into this, steam is produced, and the result is necessarily inaccurate. This inconvenience is obviated by employing high-boiling petroleum, 330—380°, which was carefully rectified, so as to obtain a specimen tolerably homogeneous. Its specific heat was determined from time to time by means of zinc, but it varied very little in the course of a series of experiments.

In the paper, the results of the experiments are given in detail, also a formula of the form—

$$q = A(t - T) + B \cdot 10^{-6}(t - T), \quad (1)$$

expressing the amount of heat required to heat 1 gram of the metal from a low temperature T (15—21°) to a higher temperature t , A and B being constants which vary with each metal. The true specific heat γ being given in another form of the formula—

$$\gamma = dq/dt = A + C \cdot 10^{-6}(t - T). \quad (2)$$

The following are the constants A and C for the various metals examined, and in columns three and four are given the specific heats

at the temperatures 50° and 300° respectively. In the original, they are given for every 50° between these limits.

	A.	C.	γ at 50°.	γ at 300°.
Cadmium	0·055107	23·78	0·0551	0·0617
Zinc	0·0915	44·4	0·0929	0·1040
Iron*	0·10912	58·064	0·1113	0·1376
Silver	0·054984	21·412	0·05556	0·06091
Copper	0·092455	21·258	0·09316	0·09846
Nickel	0·10569	94·60	0·1090	0·1327
Antimony	0·048896	16·718	0·04947	0·05366
Lead	0·02993	13·5846	0·03040	0·03380
Aluminium	0·21235	95·07	0·2164	0·2401

The following are the coefficients of the above formula reduced to—

$$\gamma = a(1 + bt),$$

the metals being arranged according to b .

	a .	$b \cdot 10^6$.
Copper	0·09205	230·8
Antimony	0·04864	343·7
Silver	0·05449	392·9
Cadmium	0·05461	433·4
Aluminium	0·2116	449·3
Lead	0·02973	456·9
Zinc	0·09070	489·5
Nickel	0·10427	907·0
Iron	0·10442	1029·1

C. E. G.

Attempt to Eliminate the Influence of the Change in the Volume of the Vessel when Measuring the Expansion of Liquids. By J. J. BOGUSKI (*Zeit. physikal. Chem.*, **2**, 482—487).—The apparatus is a modification of that used for measuring the compressibility of liquids (this vol., p. 1019), the principle being the measurement of the volume of the liquid in expansion, and in its normal condition in two separate vessels. A determination of the coefficient of expansion of amyl alcohol between 0° and 100° gave the value 0·00107732.

H. C.

Thermal Conductivity of Mercury above 100°. By A. BERGET (*Compt. rend.*, **107**, 171—172).—Experiments between 100° and 320° show that the value of the coefficient K diminishes as the temperature rises, the variation being 0·00045 for one degree.

Incidentally the author verified the law that in two walls of the

* In the case of iron, it is necessary to add a third term to equation (2), namely, $0·146574 \cdot 10^{-6}(t - T)^2$.

same nature but of different diameters, the times required to establish stationary temperatures are to one another as the squares of the diameters of the walls.

C. H. B.

Alloys of Potassium and Sodium. By A. JOANNIS (*Ann. Chim. Phys.*, **12**, 358—384).—The author determined the quantity of heat which is generated, (1) when alloys of potassium and sodium are dissolved in water, (2) when the separate metals are dissolved in water, and (3) the latent heat of fusion of the separate metals. The following are the results (in Calories) as the average of several experiments in each case:—

- (1.) Na_2K ... 44.50, NaK ... 44.06, NaK_2 ... 43.81, NaK_3 ... 44.40.
 (2.) K 45.39, Na 42.59
 (3.) K 0.61, Na 0.73

These results show that in the formation of the alloy Na_2K , there is absorption of heat, whereas in the formation of NaK there is a slight development of heat (1.20 Cal.).

The only alloy which has a definite composition is NaK_2 , the formation of which is accompanied by the development of 3.89 Cal. The development of heat (3.72 Cal.) attending the formation of NaK_3 is less than in the production of NaK_2 , showing that the former is probably a solution of potassium in the alloy NaK_2 .

F. S. K.

Sodium Glycol-oxide. By DE FORCRAND (*Compt. rend.*, **107**, 343—345).—23 grams of sodium is not completely dissolved by 62 grams of glycol even when heated for some time, and afterwards evaporated at 200° in a current of hydrogen. About one-seventh of the sodium remains undissolved. No better result is obtained by adding glycol to an alcoholic solution of sodium ethoxide.

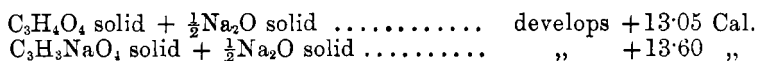
If the compound $\text{C}_2\text{H}_5\text{NaO}, 3\text{C}_2\text{H}_5\text{O}$ is mixed with one equivalent of glycol, heated in an oil-bath, and finally evaporated at 105 — 110° in a current of pure and dry hydrogen, 4 mols. of ethyl alcohol are given off, and a white residue is obtained which is not quite free from glycol. The *monosodium glycol* thus obtained does not alter in dry air, but is very deliquescent and very soluble in water. Heat of dissolution at $20^\circ = +6.01$ Cal.; heat of dissolution of glycol at the same temperature = $+1.65$ Cal. Treatment of the glycol solution with sodium hydroxide and of the sodium-derivative with sulphuric acid gave the following results:—

$\text{C}_2\text{H}_5\text{O}_2$ liq. + $\frac{1}{2}\text{Na}_2\text{O}$ solid = $\text{C}_2\text{H}_5\text{NaO}_2$	
solid + $\frac{1}{2}\text{H}_2\text{O}$ solid	develops +24.77 Cal.
$\text{C}_2\text{H}_5\text{O}_2$ liq. + NaHO solid = $\text{C}_2\text{H}_5\text{NaO}_2$	
solid + H_2O solid	„ +7.76 „
$\text{C}_2\text{H}_5\text{O}_2$ liq. + Na solid = $\text{C}_2\text{H}_5\text{NaO}_2$ solid	
+ H , gas	„ +39.65 „

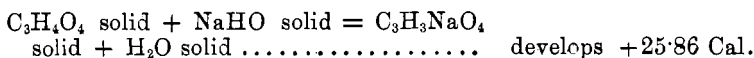
In its thermochemical behaviour, glycol is intermediate between the monhydric and trihydric alcohols.

C. H. B.

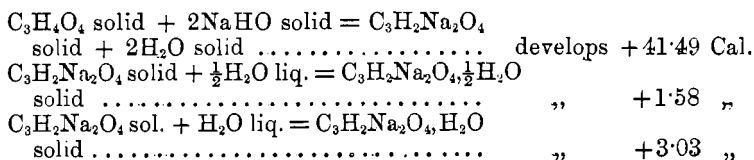
Potassium and Sodium Malonates. By G. MASSOL (*Compt. rend.*, 107, 393—395).—*Sodium malonates.*—



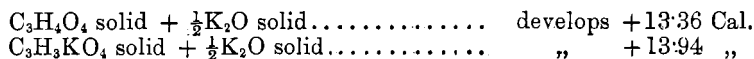
The heat of dissolution of sodium hydrogen malonate = -6.616 Cal.



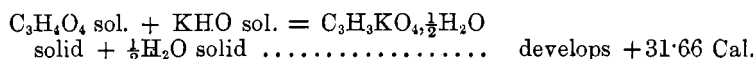
Normal sodium malonate seems to form a hydrate containing 1 mol. H_2O with a heat of dissolution $+0.13$ Cal., and another containing $\frac{1}{2}$ mol. H_2O , with a heat of dissolution $+1.5$ Cal. Heat of dissolution of the anhydrous salt = $+3.08$ Cal.



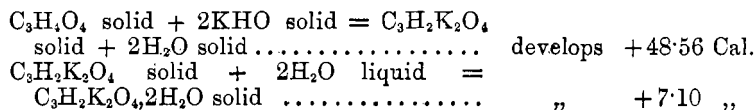
Potassium Malonates.—



The acid salt crystallises with $\frac{1}{2}$ mol. H_2O .



Normal potassium malonate crystallises with 2 mols. H_2O ; heat of dissolution = -5.0 Cal. Heat of dissolution of the anhydrous salt = $+2.10$ Cal.



In every case the thermal disturbance is less than for the corresponding reaction with oxalic acid. C. H. B.

Heat of Formation of Toluidines, Benzylamine, and Methylaniline. By P. PETIT (*Compt. rend.*, 107, 266—269).—The heats of combustion were determined by means of the calorimetric bomb, and the results are given in the following table:—

	Heat of combustion.			
	per gram.	Per gram-molecule.		Heat of formation.
		Constant pressure.	Constant volume.	
Orthotoluidine ..	9·007	964·7	963·75	3·8
Metatoluidine ..	9·015	965·6	964·6	2·9
Paratoluidine ...	8·952	958·8	957·86	9·7
Benzylamine....	9·043	968·6	967·6	0·1
Methylaniline...	9·094	974·0	973·06	-5·5

The heats of formation are calculated for the diamond and gaseous nitrogen and hydrogen. If the heat of fusion of paratoluidine is deducted, it will be seen that the heats of formation of the three toluidines do not differ by quantities sensibly greater than the error of experiment. The formation of orthotoluidine from orthocresol and ammonia with elimination of water would develop about +18 Cal.

The formation of benzylamine from benzyl alcohol and ammonia with elimination of water would develop +12·2 Cal.

It is evident that methylaniline is not analogous to the other compounds. Its formation from phenol, methyl alcohol, and ammonia, with elimination of 2 mols. H_2O , would develop +24·8 Cal., and its formation from aniline and methyl alcohol, with elimination of H_2O , would develop +15 Cal. These results explain the transformation of salts of methylaniline into salts of paratoluidine. The change of the one base into the other would develop about +15 Cal., and the union of acids with paratoluidine develops more heat than the union of the same acids with methylaniline. C. H. B.

Heat of Neutralisation of Malonic Acid. By G. MASSOL (*Compt. rend.*, **107**, 257—260).—Heat of dissolution (104 grams in 4 litres) at 20°, -4·49 Cal. Gal and Werner found -4·573 Cal. at 10°.

The heats of neutralisation in dilute solution are as follows:—

	NaHO.	KHO.	AmHO.	Ba(HO) ₂ .	Sr(OH) ₂ .	Ca(OH) ₂ .
Acid salt....	13·05	13·36	12·14	13·39	13·485	13·49
Normal salt..	13·60	13·94	12·90	16·64*	13·415	13·60
Total	26·65	27·30	25·04	30·13	26·90	27·09

It will be seen that in all cases the values are higher than those for oxalic acid, but lower than those for succinic acid.

C. H. B.

Influence of the Shape of the Bulb in Vapour-density Determinations. By H. BILTZ (*Ber.*, **21**, 2772—2776; compare Biltz, this vol., p. 1027; *Ber.*, **21**, 2016).—The following experiments were made to determine the influence of the shape of the bulb in

* Partially precipitated.

vapour-density determinations by the displacement method in cases where the substance is not completely converted into the gaseous state under the conditions of the experiment.

The vapour-density of sulphur at 518° , employing a bulb 30 cm. long and 3.3 cm. in diameter, was found to be 5.0 as the mean of many closely agreeing experiments, whereas with a bulb 26 cm. long and 7.5 cm. in diameter, the average value obtained was 4.5. Experiments with methylene bromide at 100° gave similar results; in an apparatus the bulb of which was 27 cm. long and 2.2 cm. in diameter, the vapour-density was found to be 6.4 on the average, and with a bulb 26 cm. long and 7.5 cm. in diameter, 6.1 as the average of six concordant experiments.

F. S. K.

Method of Estimating the Molecular Weight of Volatile Chlorides. By H. BILTZ (*Ber.*, 21, 2766—2772).—The author determined the vapour-density of indium chloride and ferric chloride by heating a known weight of the metal in an atmosphere of dry chlorine at a suitable temperature, and measuring the change in volume which took place. The apparatus, a modification of V. Meyer's apparatus for the determination of vapour-density, is fully described with the aid of a diagram.

The author found that at a bright red heat the vapour-density of indium chloride is 9.565, corresponding with the molecular formula InCl_3 (compare V. Meyer, *Ber.*, 12, 611; Nilson and Pettersson, *Trans.*, 1888, 816). The specific gravity of ferric chloride at 518° was found to be 9.388 as the average of three experiments. (Compare *loc. cit.*; also Grünewald and Meyer, this vol., p. 422.) F. S. K.

Hydrates of Methane and Ethylene. By VILLARD (*Compt. rend.*, 107, 395—397).—*Methane Hydrate.*—The pure gas was compressed with varying quantities of water in Cailletet's apparatus.

Temperature	0°	$+1.1^{\circ}$	5.5°	8.5°	9.9°	10.8°	14.3°
Tension in atmos.							
above normal..	26.5	30	47	63.5	75	83	123.5
Temperature			16.1°	17.3°	19.3°	20.3°	
Tension in atmos. above							
normal.....			152	178.5	232	265	

The tension is independent of the proportion of water present. The critical temperature of the hydrate is 21.5° , and it slowly decomposes at this temperature under a pressure of 300 atmos. According to Dewar the critical temperature for the gas is -99.5° .

Ethylene Hydrate.

Temperature....	0°	$+3^{\circ}$	5.5°	8°	11°	13.4°	14.8°	16.6°	17.2°
Tension in atmos.									
above normal..	6.5	8.5	11	14	21	28.5	34.5	45	59

At -18.7° the hydrate slowly decomposes under any pressure.

According to Dewar the critical point of ethylene is $+10.1$; a redetermination by the author gave $+10^{\circ}$ as the critical temperature, and 51 atmos. as the critical pressure. The critical point of ethylene itself is the same in the presence of moisture as when dry.

C. H. B.

Freezing Points of Dilute Aqueous Solutions. By F. M. RAOULT (*Zeit. physikal. Chem.*, **2**, 488—490).—The author gives the details of his experiments with those substances, for which the values of i calculated from the freezing points of the aqueous solutions differed most from those calculated by Arrhenius from the conductivity (this vol., p. 896).

H. C.

Freezing Points of Dilute Aqueous Solutions. By S. ARRHENIUS (*Zeit. physikal. Chem.*, **2**, 491—505).—The author has redetermined the freezing points of those aqueous solutions, which, using Raoult's determinations, gave numbers for i which were not in sufficient agreement with those calculated from the conductivity (preceding Abstract). The result of this work has been to bring the two into closer agreement.

H. C.

Apparent Manifestation of Chemical as Mechanical Attraction. By S. KALISCHER (*Zeit. physikal. Chem.*, **2**, 531; see this vol., p. 1009).—It is pointed out that the results obtained by Langley are in accordance with those of Faraday, who, with a cell consisting of zinc and platinum in sulphuric acid, observed that on completing the circuit a decrease in the current first occurred, and that it subsequently attained its proper value.

H. C.

The Dead Space in Chemical Reactions. By O. LIEBREICH (*Berlin. Akad. Ber.*, **43**, 959—962).—It has hitherto been assumed that chemical reaction takes place uniformly in all parts of a thoroughly mixed liquid, provided that there are no currents, and that the temperature is uniform. In this paper experiments are described which show that there may be a space in mixed solutions in which no reaction takes place. This is best shown by mixing aqueous chloral hydrate and aqueous sodium carbonate. When the solutions are suitably diluted, the chloroform which is produced separates as a fine cloud, and the time required for the reaction to commence may be varied from 1 to 25 minutes. When a test-tube is used a space from 1 to 3 mm. below the meniscus remains clear, and the lower portion of the liquid in which the reaction takes place is sharply divided from the upper by a surface curved in a direction opposite to the meniscus; this is distinct even after 24 hours. This dead space was also observed in vessels of various forms. In the case of a very small drop of the mixture, the constituents of which had been previously boiled, which was contained in a capillary tube, no reaction took place at all. When closed vessels quite full are used the reaction takes place uniformly throughout the whole, but when a full tube is closed with an animal membrane, it is possible to show the dead space. If a little of the still clear liquid is removed by means of a capillary tube and warmed, the reaction at once takes place.

Similar experiments with sulphurous and iodic acids are described. The sulphurous acid was of such a strength that 5 c.c. of the aqueous solution just decolorises 2 c.c. of a 1 per cent. permanganate solution.

The following conclusions are drawn:—(1.) In liquids the space of the chemical reaction is limited by a zone in which no reaction takes place, this zone being that portion of the liquid which is in contact with the air, or separated from the air by a thin membrane. (2.) That the reactions take place more slowly in narrow than in wide tubes. (3.) A capillary space is capable of preventing a reaction from taking place.

N. H. M.

Compression of the Moist Powder of Solid Substances and the Formation of Rocks. By W. SPRING (*Zeit. physikal. Chem.*, **2**, 532—535).—The author shows that the conglomeration of the moist powder of different chemical substances under pressure up to 6000 atmospheres is in some cases assisted, and in others retarded, by the presence of water, the quantity of the latter used in each case being 2 drops per c.c. With all metals, the action of the water is a retarding one. With soluble substances, the conglomeration is assisted for those which give a solution the volume of which is less than, and retarded for those which give a solution the volume of which is greater than the sum of the volumes of the solvent and the soluble substance. Substances belonging to the former of the above two classes have their solubility in water increased by pressure, the solubility of those belonging to the latter being decreased. Insoluble substances do not show such marked differences in the wet and dry state, but in some cases the presence of water appears to assist the conglomeration.

H. C.

Chemical Action between Substances in the Solid State. By W. SPRING (*Zeit. physikal. Chem.*, **2**, 536—538).—It is found that reactions conditioned by temperature and pressure take place between various substances in the solid state, and it appears that the particles of solid matter possess a power of diffusion similar to that of gases and liquids, although of course in much smaller degree. Thus if dry barium sulphate and sodium carbonate are mixed and compressed, a reaction sets in, which gradually spreads throughout the whole mass, and can be greatly accelerated by heat. Finely divided copper mixed with dry mercuric chloride was left to itself in a sealed tube, being only shaken from time to time in order to produce fresh contact. In four years' time the reaction was complete, and had resulted in the formation of cuprous and mercurous chlorides. In the same way dry potassium nitrate acts on dry sodium acetate, when the two are mixed in the form of powder, potassium acetate being formed. The author proposes to further investigate these changes.

H. C.

Determination of the Velocity of Etherification by Means of Electrical Conductivity. By NEGREANO (*Compt. rend.*, **107**, 173—176).—An extension of the method previously employed in the case of mixtures of acetic acid and ethyl alcohol in equal molecular proportions to mixtures containing an excess of one or the other. (Compare this vol., p. 1025.)

C. H. B.

The Energy of Compounds and the Oxides of Potassium and Lithium. By N. BEKETOFF (*Chem. Centr.*, 1888, 994, from *Bull. Acad. St. Pétersbourg*, 12, 743).—The author suggests the hypothesis that a compound of two elementary substances is stronger the nearer the proportion between the weights of the elements approaches to unity. As an example in support of this, potassium oxide is reduced by hydrogen at a low heat, whereas lithium oxide is not reduced by hydrogen or carbonic oxide. The author calculates also that the heat of oxidation of rubidium and caesium is smaller than that of potassium, and that their oxides must be reducible by hydrogen.

J. W. L.

Aspirator with Constant Flow. By O. BINDER (*Zeit. anal. Chem.*, 27, 465—466).—In aspirators of the usual form, the head of water is constantly diminishing, and the rate of aspiration is therefore not constant. But by carrying the tube conveying the gas down to the bottom of the aspirator, the effective column of water remains constant. If it be desired to diminish the action of the water on the aspirated gas, the tube may be surrounded by a larger one, open at the top, and fitted at the bottom with a narrow recurved tube; the bubbles of gas then come in contact only with the water in the wide tube. The water escape-tube should pass to the bottom of a Woulff's bottle containing a little mercury. This forms a valve, and prevents regurgitation.

M. J. S.

Safety Retort for Preparing Gases. By N. v. KLOBUKOFF (*Zeit. anal. Chem.*, 27, 467—469).—The retort consists of three parts: a cast-iron cylindrical pot, with a gutter about 2 cm. deep round its edge; a cast-iron convex cover, with a vertical rim fitting into the gutter; a wrought-iron tube screwed into the cover. The gutter is filled with a pulp consisting of 100 parts of coarse sand and 50 or 60 parts of plaster of Paris. This mixture when dry is but little penetrable by gases even under moderate pressure (30 cm. of water), but yields easily in the event of any high pressure in the retort, allowing the cover to lift, and thus preventing explosion.

M. J. S.

Lecture Apparatus for Showing Combustion of Air in Coal-gas. By G. CRAIG (*Chem. News*, 58, 55).—The apparatus consists of an inverted flask with a side-tube in the neck and an orifice at the bottom lined with asbestos; the mouth is fitted with a cork soaked in vaseline through which passes a glass tube. The flask is filled with coal-gas through the side-tube which is ignited at the orifice, the tube is pushed up through the cork, and the air will soon be seen burning from the tube with its usual feebly luminous flame in the interior of the flask.

D. A. L.

Combustion of Oxygen in Ammonia and of Hydrogen in Nitric Acid. By W. R. HODGKINSON and F. K. LOWNDES (*Chem. News*, 58, 27).—For the combustion of oxygen in ammonia, a long platinum jet about 1 mm. bore, and 8 or 9 cm. long is introduced into a flask containing 0.880 ammonia to within a cm. of the surface of the liquid, the escaping gaseous mixture is then ignited. The

oxygen burns at the jet which becomes white hot, and when immersed in the ammonia the oxygen continues to burn, generally melting the platinum tube. By regulating the pressure of oxygen, fumes of ammonium nitrite and nitrate are obtained.

When a hydrogen flame is introduced in a similar manner into a flask of nitric acid to within 2 cm. of the surface of the acid, and the pressure is adjusted so that the flame just touches the surface, the jet soon becomes white hot, and a cone of coloured flame is seen to extend from the neck of the flask to the surface of the liquid, while fumes of ammonium nitrite and nitrate escape. If the white hot point is immersed in the acid, nitrous fumes also escape, and the hydrogen continues to burn until the acid becomes considerably diluted.

D. A. L.

Inorganic Chemistry.

Reducing Action of Hydrogen in Presence of Platinum. By S. COOKE (*Chem. News*, 58, 103—106).—In these experiments, various solutions were exposed with and without platinum to the action of hydrogen prepared from pure dilute sulphuric acid, either electrolytically, or by the action of zinc. In the platinum experiments, strips of the metal as long as the tubes, and nearly as wide, are placed in tubes 300 to 400 mm. long, and about 15 mm. wide, and are held in position by a piece of platinum wire passing through the closed end of the tube. The platinum strip is coated, electrolytically, with platinum black, the tube is then filled with the solution under trial, which is subsequently displaced by hydrogen, and in this condition the tube remains in the solution. In this manner, nitric acid varying in strength from sp. gr. 1.420 to $\frac{1}{12}$ normal solution was submitted to trial; the action in dilute acids, and also in the experiments with nitrates referred to below, were aided by heating. With the strong acids, red fumes soon appear, and hydrogen is absorbed, nitrous acid being produced; with weak and dilute acids, the same action occurs in a less marked degree and at a slower rate, and ammonia is produced as well as nitrous acid. In a similar manner, potassium, sodium, barium, calcium, cobalt, nickel, lead, copper, and silver nitrates, also potassium permanganate, dichromate, and ferricyanide, and ferric chloride and sulphate, platinum chloride, mercuric chloride, and sulphuric and sulphurous acids were submitted to experiment, and likewise suffered reduction. Moreover, in the presence of the coated platinum, chlorine, bromine, and iodine combine with hydrogen in the dark; solutions of chlorine and bromine in water and iodine in potassium iodide were employed in these experiments, since with gaseous chlorine and bromine the coating frequently comes off. Hypochlorous acid and potassium chlorate are also reduced, but potassium perchlorate is not acted on. The only instances of the action of hydrogen alone on the above substances were observed in the experiments with silver nitrate,

platinum chloride, and potassium permanganate and ferricyanide, and in all cases the action was considerably slower than when in the presence of the coated platinum; it is noteworthy that the author observed no reduction when concentrated sulphuric acid or solutions of copper nitrate were exposed to hydrogen alone. Similar experiments were made with hydrogen and nitric oxide either over water or with the moist mixture over mercury. One volume of hydrogen to two volumes of nitric oxide reacted regularly in the manner represented by the equation $H_2 + 2NO = N_2O + H_2O$; equal volumes of the two gases gave a contraction equal to half the original volume, the residue being nitrogen, whereas with a large excess of hydrogen, 600 c.c. to 150 c.c. of nitric oxide, the contraction amounted to 300 c.c., the residual gas consisting almost entirely of hydrogen with a little nitrogen. All nitric oxide had disappeared, and the liquid was strongly alkaline, and contained hydroxylamine and ammonia, but no nitrous oxide. With nitric oxide in smaller proportion, the action appears pretty much the same but is slower. Nitric oxide is also reduced in a similar manner, but to a less extent, when zinc coated with copper is used instead of platinum; but with platinum, nitric oxide and carbonic oxide yield nitrous oxide and nitrogen in proportions varying with the amount of carbonic oxide used. Moreover, nitric oxide is reduced by ammonia and nitrous oxide by hydrogen, ammonia, and carbonic oxide. The platinum is more active when freshly prepared.

D. A. I.

Removal of Iodate from Iodide of Potassium. By H. N. MORSE and W. M. BURTON (*Amer. Chem. J.*, **10**, 321—322).—The solution of the iodide is boiled some little time with zinc amalgam, then filtered; the filtrate is free from zinc and mercury. The amalgam is prepared by agitating zinc-dust with mercury in presence of tartaric acid, and subsequently washing with water. Iodate of potassium is reduced by this reagent more quickly than the bromate or chlorate.

H. B.

Valency of Boron. By R. LORENZ (*Annalen*, **247**, 226—251).—As boron trioxide is exceedingly hygroscopic, an intimate mixture of the oxide with charcoal can only be obtained free from moisture by fusing boric acid and charcoal in a platinum crucible. When the mixture is in a state of quiet fusion, it is cooled and transferred to a tube of refractory glass, and heated in a current of dry carbonic anhydride to expel traces of moisture. When chlorine is passed over the mixture, boron trichloride and oxychloride and benzene hexachloride are produced. The oxychloride remains as a white, fibrous mass when the crude boron chloride is distilled. It has the composition $B_3O_{11}Cl_2$, and not $BOCl_3$ as stated by Counciler (*J. pr. Chem.* [2], **18**, 371). According to Gustavson (*Zeit. Chem.*, **6**, 521), the oxychloride $BOCl$ is formed when equivalent quantities of boron trichloride and trioxide are heated at 150° in sealed tubes. The author, however, finds that the product has the composition $2BCl_3 + 7B_2O_3$.

Boron prepared by the reduction of boric acid with sodium or

potassium is invariably mixed with a small quantity of a solid hydride of boron.

At a red heat, amorphous boron decomposes carbonic anhydride, carbon is set free, and boron trioxide is formed. As the chief argument in favour of the pentavalency of boron was the supposed existence of the oxychloride BOCl_3 , the element may now be regarded as trivalent.

W. C. W.

Boric Acid. By P. GEORGIEVIČ (*J. pr. Chem.* [2], **38**, 118—120).—In this paper the author pleads for a position for boron in the aluminium group in a periodic classification of the elements, on account of (1) its oxide acting like aluminium oxide, both as a feeble base, in such compounds as BPO_4 and $\text{B}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$, and as a feeble acid; (2) the similarity of the alkyl compounds of boron and aluminium; (3) the isomorphism of euclase and datolite.

The feeble acid character of boric acid is proved by the facts that (1) a solution of an alkaline carbonate is not decomposed by it; (2) a solution of borax is completely decomposed by a current of carbonic anhydride, and barium borate is dissolved when suspended in water through which hydrogen sulphide is passed; (3) boric acid will not liberate iodine from a mixture of potassium iodide and iodate or nitrite; (4) the red colour of ferric acetate and the violet colour of ferric chloride in solution of phenol are not bleached by boric acid; (5) boric acid is liberated from borax by the action of iodine, sodium iodide and iodate being formed.

Ostwald's avidity equivalent of 3.01 for boric acid is too high.

A. G. B.

Atomic Weight of Zinc as determined by the Composition of the Oxide. By H. N. MORSE and W. M. BURTON (*Amer. Chem. J.*, **10**, 311—321).—Pure zinc of commerce was distilled in a vacuum, using a glass tube divided into three by constrictions: from the first division the metal was distilled into the second and third divisions; when about one-fourth still remained in No. 1 division and about one-tenth had passed into No. 3 division, the operation was stopped and the process repeated four times on the contents of No. 2 division. The purified metal was found spectroscopically to be free from lead, cadmium, tin and indium. The nitric acid used for solution of the metal was distilled from glass and condensed on the outside of a platinum basin cooled by ice; thus avoiding contamination from gold solder. The solution, evaporation, and ignition were effected in porcelain crucibles, and to prevent the lids, &c., from sticking together by fusion of the glaze, this last was when necessary removed by hydrofluoric acid. The crucible was balanced by an exactly similar one which was treated with acid and ignited just as the one in actual use. After drying and heating in an air-bath, the crucibles were heated in a muffle for three hours to above the fusing point of steel. Fifteen determinations of the atomic weight varied from 65.091 to 65.119, with a mean of 65.106 ($\text{O} = 15.96$). Marignac has stated that zinc oxide dissociates at high temperatures, and that even at this temperature it still retains oxides of nitrogen. The first

statement the authors have already shown not to be true (this vol., p. 652), and the latter statement has not held in the work here described.

H. B.

Note.—The authors carefully describe the following precautions to be taken for testing for nitrogen oxides in the weighed zinc oxide: viz., removal of chlorine from the hydrochloric acid used for the solution of the sample by agitation with mercury, removal of traces of iodate from the iodide of potassium, and they remove the dissolved oxygen from the reagents by boiling, but they effect the test itself at a boiling temperature, at which the iodide of starch for which they are seeking could not possibly be formed.

H. B.

Phosphorescent Hexagonal Blende. By A. VERNEUIL (*Compt. rend.*, 107, 101—104).—The author has shown (this vol., p. 791) that zinc sulphide sublimed in a slow current of hydrogen is not phosphorescent. Natural or artificial blende distilled at an orange-red heat in pure and dry hydrogen sulphide, yields a product which is not phosphorescent. At a bright white heat, the blende sublimes somewhat rapidly even in a slow current of gas, but in this case also the sublimate is not phosphorescent. The gas which escapes from the apparatus under these conditions is a mixture of hydrogen and hydrogen sulphide containing 71 to 75 per cent. of the latter. If blende is sublimed in an atmosphere consisting of 78 per cent. of hydrogen and 22 per cent. of hydrogen sulphide, the sublimate is only slightly phosphorescent. With only 12 per cent. of hydrogen sulphide, the phosphorescence is brighter. In neither case is there a deposit of sulphur, and analysis fails to detect any difference in composition between the phosphorescent and non-phosphorescent varieties.

When non-phosphorescent blende is distilled at an orange-red heat in an atmosphere of nitrogen, a minute trace of hydrogen sulphide escapes. If the same blende is heated at 400° in a vacuum, a small quantity of the same gas is evolved, and hence it would seem to be occluded in the blende. The sublimate obtained in nitrogen has a feeble white phosphorescence even if sublimation is effected at a bright white heat. Blende mixed with 5 per cent. of zinc oxide or 1 or 2 per cent. of carbon from sugar, and sublimed, yields a sublimate which shows a brilliant phosphorescence. The same result is obtained in a neutral atmosphere if the sublimate is cooled rapidly in order to prevent the re-combination of any products of dissociation. From these results it follows that wurtzite formed by sublimation becomes very phosphorescent only when the original blende has been in contact at a high temperature with some desulphurising agent. The phosphorescence is brighter the lower the temperature at which the wurtzite is formed.

C. H. B.

Observations on Sabatier's Papers on Hydrochlorides of Cupric and Cobalt Chlorides. By ENGEL (*Compt. rend.*, 107, 178—179).—The author points out that Sabatier's and his own results are not contradictory, but prove the existence of two hydrochlorides of cupric chloride, just as in the case of zinc chloride. He claims

priority in the discovery of the hydrochloride of cobalt chloride. (Compare this vol., pp. 558, 1036, 1037.) C. H. B.

Basic Cupric Chromate. By L. BALBANO (*Chem. Centr.*, 1888, 1024, from *Rend. Acad. Lincei* [4], 4, 597—600).—A solution of cupric sulphate is not completely precipitated by neutral ammonium chromate, the complete precipitation only being effected by the addition of ammonia. Both the precipitate first produced by the ammonium chromate and that by the later addition of the ammonia have the same composition, $\text{Cu}_3\text{CrO}_6 + 2\text{H}_2\text{O}$.

By evaporating the aqueous solution on the water-bath, an amorphous mass is formed. Alcohol precipitates from the aqueous solution a dirty green precipitate, and is at the same time oxidised to acetic acid. J. W. L.

Action of Petroleum on Lead. By W. Fox (*Chem. News*, 58, 39).—The lead lining of tanks in which petroleum is stored soon becomes corroded, and a brownish powder forms consisting of lead hydroxide, carbonate, and a little valerate and some organic matter. When lead is heated in a sealed tube with petroleum free from acid, no gas is evolved and lead oxide alone is formed; if a little valeric acid is added to the petroleum and oxygen is excluded from the tube, then lead hydroxide and carbonate form; heated in a similar manner with valeric acid in the presence of oxygen, the lead forms hydroxide and carbonate and oxygen is absorbed. The author therefore thinks that the formation of lead carbonate in the petroleum tanks is due to the action of an oxidising agent, and a small quantity of valeric acid present in the petroleum. D. A. L.

Yttrium Compounds. By A. DUBOIS (*Compt. rend.*, 107, 99—101 and 243—245).—3 parts of pure yttria from the oxalate, 1 part of amorphous silica, and 30 parts of calcium chloride were heated together for two hours in a wind furnace and the cooled product was treated with water. In this way a silicate, $\text{Y}_2\text{O}_3\cdot\text{SiO}_2$, analogous to gadolinite, is obtained in microscopic, highly bi-refractive, monoclinic crystals, which are attacked by acids. Some measurements of the faces and angles are given. The artificial crystals differ from those of gadolinite in their angle of extinction and in the separation of the optical axes, the differences being doubtless due to the presence in gadolinite of oxides other than yttria.

In the preparation of yttrium silicates by Lechartier's method, a mixture of cubes and elongated prisms is obtained, and if this is fused with sodium carbonate and the product treated with acids, the prisms, which consist of a double silicate of calcium and yttrium, are decomposed and dissolved, whilst the cubic crystals which consist of yttrium oxide remain unaltered.

When amorphous yttrium oxide is heated to redness with calcium chloride for about two hours, and the product is extracted with warm water, highly refractive crystals of yttrium oxide are obtained, and these are attacked with difficulty by acids or by fused sodium

carbonate. The crystals are trapezohedrons resembling those of analcime, but they have no action on polarised light.

Yttrium oxide heated to redness on a gas-carbon support in a current of chlorine and carbonic oxide yields yttrium chloride in confused lamellæ, very soluble in water, with formation of the very hygroscopic hydrate $Y_2Cl_6 + 12H_2O$, described by Cleve. In the preparation of the chloride, care must be taken that the current of gas is not too rapid, otherwise a considerable quantity of the salt is volatilised. If the tube is heated to 1100° , the chloride melts, and distinct crystals of considerable size can be observed floating on the surface of the liquid. The crystals are not affected by benzene. They are transparent, colourless, highly bi-refractive, rectangular lamellæ with transversal cleavage. The bisectrix is negative, and the separation of the optical axes is about 50° .

Yttrium bromide is obtained in a similar manner. It closely resembles the chloride in appearance, is very deliquescent, and with water forms the hydrate $Y_2Br_6 + 18H_2O$, described by Cleve.

If dry hydrogen sulphide is passed over a mixture of anhydrous yttrium chloride with excess of sodium chloride, heated at 1000° in a boat of gas-carbon, a greenish, crystalline product is obtained, and when this is treated with water, transparent, greenish lamellæ of the compound, Na_2S, Y_2S_3 , are left undissolved. The crystals do not alter at the ordinary temperature, but burn if heated to redness. They are not affected by warm water, but are dissolved even by dilute acetic acid. The form of the crystals is a hexagonal prism flattened in a direction perpendicular with the principal axis, with three directions of cleavage parallel with the sides of the basal hexagon, but the symmetry of the crystals is not perfect, owing to the presence of impurities.

C. H. B.

Production of Metallic Chlorides from Oxides. By A. FAURE (*Compt. rend.*, **107**, 339—340).—The oxide, such as bauxite, is heated directly by means of the flame from a regenerative furnace, and when the temperature is sufficiently high, the flame is cut off, and a mixture of hydrogen chloride and naphthalene vapour is passed into the heated material. These gases are completely utilised in the conversion of the oxide into chloride, and have little or no injurious action on the bricks of the furnace.

The mixture of hydrogen chloride and naphthalene alone is not decomposed even at a bright white heat, or at any rate no substance is formed which condenses at temperatures above 100° .

C. H. B.

Vapour-density of Gallium Chloride. By C. FRIEDEL and J. M. CRAFTS (*Compt. rend.*, **107**, 306—309).—Carefully sublimed gallium chloride was volatilised in an atmosphere of nitrogen. Direct experiment proved that no chlorine was liberated. The following results were obtained :—

Temperature	237°	307°	357.15°	377.6°
Vapour-density ..	11.73	10.61	9.08	7.82

The values previously obtained by L. de Boisbaudran were—

Temperature	247°	273°	357°	440°
Vapour-density ..	13·4	11·9	10·0	7·8

It follows that up to 273° gallium chloride has the formula Ga_2Cl_6 , but beyond this temperature the molecule dissociates into 2GaCl_3 . (Compare Nilson and Petterssen, *Trans.*, 1888, 824.) In the group containing aluminium, gallium, indium, the tendency of the chloride to dissociate into simpler molecules at higher temperatures increases as the atomic weight increases. The gallium chloride employed by the authors was not absolutely dry, and hence the values obtained are somewhat too low.

Experiments by the diffusion method prove that when aluminium chloride is strongly heated in an atmosphere of nitrogen, no chlorine is liberated, and hence the decrease in vapour-density must be due to the dissociation of Al_2Cl_6 into 2AlCl_3 . (Compare this vol., p. 1040.)
C. H. B.

Vapour-density of Chlorine and Ferric Chloride. By C. FRIEDEL and J. M. CRAFTS (*Compt. rend.*, 107, 301—306).—The authors have previously shown (this vol., p. 1040) that the vapour-density of aluminium chloride is constant between 288°, and 400° and corresponds with the formula Al_2Cl_6 . Deville and Troost's experiments with ferric chloride gave results corresponding with the formula Fe_2Cl_6 , but the later determinations of V. Meyer and Grunewald have shown that between 440° and 1300° the vapour-density is always lower than that corresponding with Fe_2Cl_6 , and agrees more nearly with the formula FeCl_3 . There is always, however, a want of agreement between the observed and calculated values, because at temperatures above 518° the ferric chloride decomposes into ferrous chloride and chlorine. The authors point out that Meyer's results do not agree at all well with the formula FeCl_3 , and consider that above 750° the ferric chloride dissociates into Fe_2Cl_4 and Cl_2 , whilst the further reduction of density observed above 1052° is due to the partial dissociation of Fe_2Cl_4 into 2FeCl_2 . The boiling point of ferrous chloride and its vapour-density are, however, not yet known.

The modification of Dumas' apparatus employed by the authors makes it easy to ascertain whether dissociation has taken place and any crystals have been deposited. They find that, contrary to the statement of Meyer and Grunewald, ferric chloride in an atmosphere of nitrogen is dissociated into chlorine and ferrous chloride, the latter being deposited in almost colourless crystals which do not recombine with the liberated chlorine on cooling, nor after remaining in contact with it at the ordinary temperature for several days. The ferrous chloride is not volatile at 440°, and hence the volume of gas in the apparatus is not altered in consequence of the dissociation.

In order to prevent the dissociation, the apparatus was filled with chlorine, and hence it became necessary to determine the relative density of this gas at the temperatures employed. The chlorine was made in some experiments from manganese peroxide and hydrochloric acid, in others from potassium dichromate and hydrochloric

acid, and was dried by means of sulphuric acid. The following results were obtained :—

Temperature	19.7°	21.6°	23.0°	356.9°	440.0°
Sp. gr.....	2.479	2.458	2.475	2.451	2.448

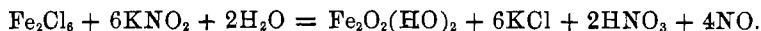
Between 21° and 357° the coefficient of expansion of chlorine is to that of air as 1.009 : 1.000.

The experiments with ferric chloride were made in the same way as those with aluminium chloride. Relatively low temperatures were employed, and the quantity of the salt used was such that chlorine was always present in considerable excess. The ferric chloride volatilised completely and not a trace of ferrous chloride was formed. Ferric chloride boils at 280—285°, and melts under pressure at 301°. The following results were obtained :—

Temperature ..	321.6°	325.2°	356.9°	357.0°	442.2°	442.2°
Vapour-density.	11.41	12.47	12.04	11.85	11.66	11.30

Between 321° and 442° the vapour-density is practically constant, and corresponds with the formula Fe_2Cl_6 . C. H. B.

Action of Potassium Nitrite on Ferric Chloride. By L. PESCI (*Chem. Centr.*, 1888, 1023—1024, from *Ann. Chim. Farm.* [4], 7, 305—307).—Ferric chloride and potassium nitrite react together with evolution of nitric oxide, whilst a brownish-red precipitate forms. In a flask, from which the air had been displaced by means of carbonic anhydride, a solution of potassic nitrite was introduced and then one of ferric chloride. After the evolution of nitric oxide ceased, the colourless liquid was separated from the brown precipitate, and the excess of nitrous acid destroyed by carbamide and acetic acid, and finally concentrated sulphuric acid was added, when the presence of nitric acid was ascertained. The reaction may probably be represented by the following equation :—



The brown precipitate of the reaction, probably metaferric hydrate, is best separated by dialysis. It is soluble in water, and behaves entirely differently from the ferric salts. With ferrocyanide, a brown coloration is first formed, which eventually develops into a precipitate. Ferricyanide and thiocyanate give no precipitate. Tannin gradually produces a brown precipitate. A trace of a salt of alkali or sulphuric acid coagulates the oxide immediately. A very small quantity of nitric acid does not precipitate the solution, but the concentrated acid precipitates ferric oxide, which, after some time, gradually dissolves. Carbonic anhydride does not precipitate the oxide. By boiling the solution of this hydrate, a reddish brown precipitate forms, which, however, redissolves on cooling. Phenolphthaleïn and rosolic acid show an acid reaction in the solution. The solution is very stable.

J. W. L.

Crystallised Hydrated Potassium Ferrite prepared in the Dry Way. By G. ROUSSEAU and J. BERNHEIM (*Compt. rend.*, 107,

240—243).—When potassium ferrate is thrown into fused potassium chloride or hydroxide, it decomposes rapidly into potassium ferrite and oxygen. The alkalinity of the flux has no influence on the result as in the case of barium ferrate. If potassium hydroxide is used, the ferrite is not changed by continued heating to bright redness, but if the flux is a mixture of the hydroxide and chloride, the ferrite is gradually converted into reddish, transparent crystals similar to those of sodium ferrite.

When potassium ferrite, obtained by Mitscherlich's method of heating potassium ferric oxalate, is heated to redness with potassium chloride or a mixture of the chloride and hydroxide, it yields red-brown crystals of the same composition as those just described. 5 grams of potassium ferrite fused with 30 grams of potassium chloride and the same quantity of the hydroxide, gave crystals of the composition Fe_2O_3 , 86.52; H_2O , 11.34; K_2O , 2.91. When the heating was continued until the greater part of the flux was volatilised, the product had the composition Fe_2O_3 , 90.16; H_2O , 5.76; K_2O , 3.73, and hence it is evident that the hydrate first formed was afterwards decomposed.

Better results were obtained by using the semi-crystallised ferrite prepared according to Salm-Horstmar's method of fusing ferric hydroxide with 4 parts of potassium carbonate. This product was mixed with twice its weight of potassium chloride, and carefully heated until most of the latter had volatilised. In this way, comparatively large, transparent, red-brown crystals were obtained. Three different specimens gave the following results:—

Fe_2O_3	85.46	86.34	84.67
H_2O	10.82	11.11	10.94
K_2O	3.57	3.01	3.95

This compound is soluble in mineral acids, but if calcined it acquires an alkaline reaction, and then dissolves slowly even in concentrated boiling hydrochloric acid. It loses 5.08 per cent. of water at $150-160^\circ$, 3.45 per cent. at about 300° , and the remainder at a red heat. These facts point to the existence of three distinct hydrates.

If crystallised ferrous sulphate is heated to redness with an equal weight of potassium chloride for half an hour, one of these hydrates is obtained in brilliant lamellæ of the composition Fe_2O_3 , 84.33; H_2O , 11.45; K_2O , 3.66. If heating is continued for an hour, the potassium chloride is completely volatilised, and the crystals obtained have the composition Fe_2O_3 , 97.20; H_2O , 1.47; K_2O , 1.08. Further heating would doubtless result in the formation of hematite.

It is noteworthy that the water and potassium oxide volatilise simultaneously, a fact which affords further proof that in these compounds they have a similar function. C. H. B.

Chinese Treatment of Cobalt Ores. By T. I. BOWLER (*Chem. News*, 58, 100).—The ore (a sample examined contained per cent., 35 of Fe, 13.1 of Mn, 3.5 of Ni, 2.4 of Co, all as oxides, and 46 per cent. of gangue) is washed, powdered while wet, and allowed to settle in water; the lower layers are then dried, mixed with borax,

and fused up with glass. After 36 or 40 hours, the glass is light blue in colour with a tint of amethyst due to manganese, but colours due to iron or nickel are scarcely apparent: the bottom portion of the melt is worthless. For painting on porcelain, the Chinese frit this same ore with felspar, white kaolin clay, and much borax. D. A. L.

Dissociation of Fused Metallic Sulphides. By T. S. HUNT (*Chem. News*, **58**, 8^r).—Referring to Moore's note on the separation of a brilliant, ductile, metallic alloy from nickel regulus (*Abstr.*, 1887, 1081), the author points out that he has described the separation of metallic iron from a copper-iron regulus. The fused mass consisted of oxysulphides, and on cooling decomposed into iron, magnetite and sulphides. The separation of copper from rich copper regulus is another instance of this decomposition of sulphides which are only stable at high temperatures. A crystalline subsulphide, $\text{Fe}_3\text{Ni}_2\text{S}$, is found in cavities in the nickel matte smelting hearth in Pennsylvania. D. A. L.

Zinc Titanates. By L. LÉVY (*Compt. rend.*, **107**, 421—423).—A *bibasic titanate*, $\text{TiO}_2, 2\text{ZnO}$, is obtained by heating to bright redness in a brasqued crucible a mixture of 2 parts of titanic oxide, 15 parts of zinc sulphate, and 15 parts of potassium sulphate. It forms black, crystalline grains; sp. gr. at $20^\circ = 4.16$. It is decomposed by chlorine but not by hydrogen, and is dissolved by hot and dilute or cold and concentrated acids and alkalis, and also by a fused mixture of potassium nitrate and sodium carbonate. It can also be obtained by heating the sesquitanate with excess of zinc sulphate or choride.

A *sesquitanate*, $2\text{TiO}_2, 3\text{ZnO}$, is obtained by heating to redness a mixture of 1 part of titanic oxide, 5 parts of zinc sulphate, and 1.2 parts of potassium sulphate, and washing the product with dilute sulphuric acid. It forms a yellow, crystalline powder, which is not decomposed by heat. It is decomposed by chlorine or hydrogen, and slowly by warm sulphuric or nitric acid, or a mixture of sulphuric and hydrofluoric acids. It is completely dissolved by cold hydrochloric acid, and is decomposed by fused potash, but not by a mixture of potassium nitrate or sodium carbonate.

The *normal titanate*, TiO_2, ZnO , is obtained in a similar manner from a mixture of titanic oxide, 2 parts; zinc sulphate, 8 parts, and potassium sulphate 3 parts. It is a pale-violet substance with a conchoidal fracture, and not unfrequently forms silky needles; sp. gr. at $20^\circ = 3.17$. It is decomposed by chlorine, but not by hydrogen. Boiling acids and concentrated potash attack it with difficulty, but it is slightly attacked by a fused mixture of potassium nitrate and sodium carbonate, and is decomposed by fused potash.

An *acid titanate*, $5\text{TiO}_2, 4\text{ZnO}$, is formed at a cherry-red heat from a mixture of titanic oxide, 3 parts; zinc sulphate, 12 parts, and potassium sulphate, 1 part; the product being washed with dilute nitric acid. It forms small, pale-brown, crystalline leaflets, sp. gr. at $19^\circ = 3.68$. It is insoluble in all ordinary solvents, and is decomposed by chlorine, but not by hydrogen. It is not attacked by concentrated acids in the

cold, but is dissolved by all except hydrochloric acid when heated, and is also dissolved by fused potassium hydrogen sulphate.

The nature of the product is determined by the temperature and by the composition of the mixture. At a dull red heat, the sesquitanate is always formed, but at higher temperatures one of the other compounds is formed according to the composition of the mixture, the proportion of potassium sulphate being of great importance. It is probable that a potassium titanate is first formed, but is subsequently decomposed by the zinc salt. In fact, the zinc compounds can be obtained by the direct action of zinc sulphate on potassium titanate.

C. H. B.

Fluorine-derivatives of Pertitanic Acid. By A. PICCINI *Gazzetta*, 17, 479—486).—In a communication to the *Arcademia dei Lincei* (Sept., 1885), the author described a barium fluoroxypertitanate, ($\text{TiO}_2\text{F}_2, \text{BaF}_2$), prepared by adding barium nitrate to a solution of the octahedral ammonium fluoroxypertitanate, when it comes down as a flocculent precipitate. Sometimes also, under conditions which are not accurately known, this was accompanied by a crystalline barium compound, probably $2\text{TiO}_2\text{F}_2, 3\text{BaF}_2$, corresponding with the octahedral ammonium salt.

When the amorphous barium salt is gently heated, it loses its yellow colour and becomes white, but at a higher temperature it parts with its fluorine, and is converted into a white mass of the composition BaO, TiO_2 ; the total loss being somewhat more than 20 per cent. of the original weight.

In order to ascertain what was the nature of the reaction which takes place in the first stage, some of the barium fluoroxypertitanate was heated in a vacuum at 150 — 160° , the gas which was given off collected, and the residue weighed. The gas evolved was pure oxygen, and the residue had the composition TiOF_4, Ba , the decomposition taking place according to the equation $2(\text{TiO}_2\text{F}_2, \text{BaF}_2) = 2\text{TiOF}_4, \text{Ba} + \text{O}_2$. As the residue is easily soluble in dilute acids, it cannot be a mixture containing titanic acid, and is therefore probably a new barium salt of the formula $\text{TiOF}_2, \text{BaF}_2$.

Fluoroxypertitanic acid, $\text{TiO}_2\text{F}_2, 2\text{HF}$, may be obtained in solution by adding barium fluoroxypertitanate, in slight excess, to well-cooled dilute sulphuric acid (4—5 per cent.) contained in a platinum dish, filtering (using a silver funnel) from the barium sulphate and excess of fluoroxypertitanate, and cautiously precipitating the traces of barium in solution with dilute sulphuric acid. If an alkaline carbonate is added to the liquid, it effervesces and deposits yellow peroxide of titanium, but on cautiously neutralising with potassium hydroxide, a crystalline precipitate of potassium fluoroxypertitanate, $\text{TiO}_2\text{F}_2, 2\text{KF}$, is obtained; the ammonium salt could not be obtained definitely crystallised. On saturating the acid with ammonia and adding ammonium fluoride, the octahedral ammonium fluoroxypertitanate, $\text{TiO}_2\text{F}_2, 3\text{NH}_4\text{F}$, is thrown down in the crystalline state. That the solution really contained an acid of the formula given above was confirmed by determining the relation between the titanium and fluorine.

The author has been unable to obtain any zirconium compounds corresponding with those of titanium just described. C. E. G.

Amorphous Antimony. By F. HÉRARD (*Compt. rend.*, 107, 420).—When antimony is heated to dull redness in a current of nitrogen, greyish vapours are evolved, which condense on the cool parts of the tube in agglomerations of small spheres similar in appearance to Betten-dorff's amorphous arsenic. The sublimate contains 98·7 per cent. of antimony, and is similar to the amorphous antimony obtained by Gore by the electrolysis of the haloïd salts. It melts at 614° ; sp. gr. at $0^{\circ} = 6\cdot22$. Ordinary crystallised antimony melts at 440° ; sp. gr. = $6\cdot73$. The fact that the amorphous variety is not produced in a current of hydrogen seems to indicate that a nitride is first formed, but decomposes in the cooler parts of the tube. C. H. B.

Bismuth and Lithium in Iron and Slags. By H. N. WARREN (*Chem. News*, 58, 27).—Hydrogen sulphide produced a decided black precipitate of bismuth sulphide in hydrochloric acid solutions containing 5 grams of some Cleveland district ordinary blast slags, in six samples out of nine. Estimated in the usual way, the amount was from 0·1 to 0·5 per cent. of bismuth oxide in the different samples; the corresponding samples of iron contained 0·01 to 0·04 per cent. of metallic bismuth. The slags were also found to contain from 0·05 to 0·01 per cent. of lithium estimated as carbonate, which was also detected spectroscopically in the residue obtained from four samples of cast iron out of six, after removal of the iron and other substances.

D. A. L.

Halogen Compounds of Gold. By G. KRÜSS and F. W. SCHMIDT (*J. pr. Chem.* [2], 38, 77—84; compare this vol., p. 28).—The authors have again failed to obtain a chloride of gold having the constant composition Au_2Cl_3 , notwithstanding that they have exactly followed Thomsen's latest directions (this vol., p. 559). The product of the action of chlorine on gold is a mixture of auric chloride and unaltered gold, for the former may be dissolved away from the latter by water and by ether. Nor is the compound Au_2Br_3 obtained by the action of bromine on gold; when the absorption of bromine ceases, the product is auric bromide mixed with a trace of unaltered gold. Only a small quantity of the gold can be converted into auric bromide by bromine vapour. A. G. B.

Rhodium Salts. By E. LEIDIE (*Compt. rend.*, 107, 234—237).—If a saturated solution of ammonium chloride is added to a concentrated solution of ammonium rhodium chloride containing a considerable proportion of free nitric acid, crystalline plates resembling chromic chloride are deposited. When these are dried in a vacuum, they have the composition $\text{Rh}_2\text{Cl}_6\cdot 6\text{NH}_4\text{Cl}\cdot 2\text{NH}_4\text{NO}_3$. If treated with water, they decompose into the double chloride $\text{Rh}_2\text{Cl}_6\cdot 6\text{NH}_4\text{Cl} + 3\text{H}_2\text{O}$, rhodium chloride, and gaseous products similar to those produced by the action of aqua regia on ammonium chloride. The feeble solubility of this compound must be borne in mind when ammonium chloride is employed to separate rhodium from platinum.

Rhodium sulphate, $\text{Rh}_2(\text{SO}_4)_3$, is obtained by dissolving rhodium sesquioxide in excess of sulphuric acid, evaporating to a syrup, and finally heating at 440° until the weight is constant. At this temperature, the whole of the free acid is expelled, but the sulphate is not decomposed. It forms a brick-red, non-hygroscopic powder, stable in presence of water if the latter does not exceed 16 equivalents per equivalent of salt, but decomposed by a larger quantity with formation of a basic sulphate and free sulphuric acid. When boiled with large quantities of water until the washings are no longer acid, it yields a subsulphate, $\text{Rh}_2(\text{SO}_4)_3 \cdot \text{Rh}_2\text{O}_3$. Rhodium sulphate forms no alums and no crystallisable double sulphates.

The *double oxalates* have the general formula $\text{Rh}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{M}_2\text{C}_2\text{O}_4 + n\text{H}_2\text{O}$, crystallise readily, and are analogous to but not isomorphous with the double ferric and chromic oxalates. *Rhodium potassium oxalate* is obtained in garnet-red, triclinic prisms, very soluble in water, by dissolving freshly precipitated rhodium sesquioxide in a solution of potassium hydrogen oxalate and crystallising in a vacuum. In a concentrated solution, the ordinary reactions of rhodium and oxalic acid are partially masked; in dilute solutions, the salt is decomposed with precipitation of rhodium sesquioxide. The sodium and ammonium salts have similar properties, and are obtained in a similar manner. The former crystallises with 12 mols. and the latter with 9 mols. H_2O . *Rhodium barium oxalate*, obtained by the action of barium chloride on the potassium salt, forms orange-yellow crystals, which contain 6 mols. H_2O and are only slightly soluble in boiling water.

C. H. B.

Note by Abstractor.—The fact that in solutions of these so-called double oxalates the reactions of rhodium and oxalic acid are partially masked seems to indicate that these compounds are really rhodio-oxalates, analogous in constitution to the chromoxalates.

C. H. B.

Mineralogical Chemistry.

Cobalt Ores. By G. VOLLHARDT (*Zeit. Kryst. Min.*, **14**, 407—408).—Crystals of smaltine and cloanthite when cut and treated with acids exhibit a series of zones of varying solubility. In order to determine whether this is due to varying composition, specimens of ore were powdered and treated with hydrochloric acid and potassium chlorate. A portion was thus dissolved, and of the residue a portion was used for analysis and a portion treated in the same way, the final residue being analysed. The results were as follows :—

	Ia.	Ib.	Ic.	Id.	IIa.	IIb.	IIIa.	IIIb.
SiO ₂	0·14	0·12	0·13	0·16	—	—	—	—
S	0·61	0·61	(0·61)	(0·61)	0·30	(0·30)	—	—
Bi.....	0·31	0·41	0·16	0·18	4·58	0·37	—	—
Pb	0·37	0·36	0·01	0·12	—	—	—	—
As	75·53	73·46	75·78	76·19	71·19	75·43	77·94	78·26
Fe	0·37	0·38	0·47	0·30	1·35	1·22	5·07	6·69
Ni	21·94	{ 19·88 2·03 }	{ 19·89 2·30 }	21·71	21·84	22·24	{ 12·01 3·69 }	15·05
Co								
Totals ...	99·27	97·25	99·35	99·27	—	—	—	—

I. Cloanthite from Schneeberg in Saxony: *a* and *b*, original ore; *c*, first residue; *d*, second residue. II. Cloanthite crystals, cubes with pentagonal dodecahedra, from Wolkenstein in Saxony: *a*, original ore; *b*, residue. III. Cloanthite from Markirch in Alsace, sp. gr. 6·32.

The results obtained with the Schneeberg cloanthite (I), showing that for the most part a compound poor in arsenic has been dissolved, are confirmed by the fact that the compound CoAs₃ (skutterudite) is soluble with considerably greater difficulty than smaltine and cloanthite. Whether an admixture of RAs₃ or of free arsenic is present in the latter minerals cannot be determined. In the cloanthite from Wolkenstein (II) the ratio of R to As has increased from 1 : 2·4, in the residue to 1 : 2·62. The bismuth appears not to be in combination with the metals. The Alsatian cloanthite (III) when treated with acid was found to be homogeneous. It has the formula RAs₃, whilst other crystals from the same locality previously analysed gave the formula RAs₂. The author concludes that further investigations are necessary to determine the chemical composition of smaltine and cloanthite.

B. H. B.

Calciostrontianite (Emmonite) from Brixlegg. By A. CATHEIN (*Zeit. Kryst. Min.*, **14**, 366—374).—A mineral occurring in small, well-developed, rhombic crystals on barytes in the Grosskogel grey copper mine at Brixlegg in the Tyrol, was first thought to be smithsonite, and subsequently strontioalcite. It gave on analysis the following results:—

SrCO ₃ .	CaCO ₃ .	Total.
86·89	13·14	100·03

The mineral is therefore a calciostrontianite having the formula 9SrCO₃, 2CaCO₃. It is identical with the American mineral named emmonite by T. Thomson in 1836. As the barytes matrix contains 0·71 per cent. of strontium sulphate and 0·1 per cent. of calcium sulphate, the calciostrontianite may have been formed from this by the action of water containing carbonic acid.

B. H. B.

Phosphorite of Capo di Leuca. By I. GIGLIOLI (*Gazzetta*, 18, 54—56).—This phosphorite occurs abundantly in the pliocene limestone of Capo di Santa Maria di Leuca, at Otranto. It is found in nodules and fragments, which are very hard, and can readily be separated from the calcareous gangue by calcining the lumps in a furnace and then treating them with cold water. As yet no technical use has been made of this bed of phosphorite.

The results of the analysis are as follows:—

$\text{Ca}_3(\text{PO}_4)_2$.	CaCO_3 .	CaSO_4 .	Fe_2O_3 .	Silica.	Al_2O_3 , &c., by difference.	H_2O .
39.22	39.84	1.81	4.02	3.88	12.98	1.25
C. E. G.						

Arnimite. By A. WEISBACH (*Zeit. Kryst. Min.*, 14, 399—400, from *Jahrb. Berg. Hüttenw. K. Sachsen*, 1886, 86).—The name of arnimite is applied by the author to a mineral occurring in the so-called porcelain-jasper of Planitz near Zwickau. Under the microscope, this mineral is seen to be an aggregate of short, acicular crystals. A specimen, as free as possible from the accompanying anhydride and gypsum, gave on analysis the following results (I):—

	CuO.	SO_3 .	Fe_2O_3 , Al_2O_3 .	CaO.	H_2O .	Total.
I.	56.81	24.43	0.35	0.56	(17.85)	100.00
II.	49.96	24.59	—	8.17	17.76	100.48

These results are in fair accord with the formula $\text{Cu}_5\text{S}_2\text{O}_{11} + 6\text{H}_2\text{O}$. As this composition approaches most nearly to that of herrngrundite, a new analysis was made of that Hungarian mineral, the results of which (II) lead to the formula $\text{Cu}_4\text{CaS}_2\text{O}_{11} + 6\text{H}_2\text{O}$, showing that herrngrundite is a lime-bearing arnimite.

B. H. B.

Minerals of the Tetragonal System present in Crystallised Slags. By J. H. L. VOGT (*Chem. Centr.*, 1888, 985, from *Berg. Hütt. Zeit.*, 47, 187—189).—The author contends that his former assertion concerning the identity of certain crystalline minerals found in slags with the natural melilite and gehlenite is supported by the optical properties and structure of the minerals. He has also noticed in the blast furnace slags another mineral in which lime is the principal base, apparently closely related to melilite.

J. W. L.

Alteration of Quartz into Talc. By E. WEINSCHENK (*Zeit. Kryst. Min.*, 14, 305—323).—The extensive talc deposit of Göpfersgrün in the Fichtelgebirge occurs at the contact of granite and crystalline schists, consisting of mica-schist, phyllite, and, more rarely, serpentine, variolite, and chlorite-schist. It forms part of a limestone bed in which occur quartz in crystals and grains, fluorspar, chondrodite, magnetic pyrites, iron pyrites, garnet, phlogopite, grammatite, graphite, and many other minerals. The talc deposited on the limestone contains pseudomorphs of talc after brown spar and quartz, and more rarely of talc after calcite, and of chalcedony after dolomite. The following analyses indicate the purity of the talc:—

	SiO ₂ .	MgO.	Fe ₂ O ₃ .	H ₂ O.	Total.
I.	63·52	31·72	—	4·76	100·00
II.	62·87	31·62	1·31	3·93	99·73
III.	63·32	31·49	0·57	4·38	99·76
IV.	62·98	31·36	1·85	4·32	100·51

I is the composition of pure talc calculated from the formula $\text{Mg}_3(\text{SiO}_3)_4\text{H}_2$; II is the composition of a yellowish-white pseudomorph after quartz; III of a pure white dolomite pseudomorph, and IV of ordinary greenish talc.

The process of the alteration of the quartz into talc was elucidated by a microscopical examination of the quartz occurring in the rock immediately above the talc bed, where every stage of the transition can be distinctly seen.

B. H. B.

Artificial Magnesia Mica. By J. H. L. VOGT (*Chem. Centr.*, 1888, 985, from *Berg. Hütt. Zeit.*, **47**, 197—199).—A magnesia mica nearly always crystallises out of the copper slag of the Kafveltorp copper works in Sweden, which is but slightly different from the natural mineral, and has a composition agreeing with the proportions $\text{Si} : \text{Al} : \text{Mg} (+ \text{Fe}) : \text{K} (+ \text{Na}) = 1·017 : 0·336 : 1·00 : 0·384$, whereas these are $1 : 0·4 : 1 : 0·4$ in the natural mineral. It would appear that the presence of fluoride in the slag is a necessary condition to the formation of the mica.

J. W. L.

Biotite from Christiania. By P. JANNASCH (*Zeit. Kryst. Min.*, **14**, 400).—In a Norwegian journal, the author gives the following analysis of the brown biotite from the micaceous rock that forms a portion of the contact zone in the Silurian basin of Christiania :—

SiO ₂ .	TiO ₂ .	Nb ₂ O ₅ .	Al ₂ O ₃ .	FeO.	MgO.	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
33·95	3·40	0·98	17·69	21·94	7·98	1·10	1·00	8·39	3·46	99·89

Traces of manganese, strontium, and lithium were also observed. The analytical results correspond with the empirical formula $\text{R}'_{18}\text{R}''_{15}\text{R}'''_{10}\text{Si}_{18}\text{O}_{75}$.

B. H. B.

Cronstedtite from Kuttenberg in Bohemia. By K. VRBA (*Zeit. Kryst. Min.*, **14**, 410, from *Sitzber. Böhm. Ges. Wiss.*, 1886).—At Kuttenberg, cronstedtite has been found in black, fibrous masses on cryptocrystalline, opaque quartz, or on a granular mixture of quartz, pyrites, and blende. The mineral has a sp. gr. of 3·445, and on analysis gave the following results :—

SiO ₂ .	Fe ₂ O ₃ .	FeO.	MnO.	H ₂ O.	Total.
17·34	43·05	30·27	0·16	(9·18)	100·00

Formula, $\text{H}_3\text{Fe}'_3\text{Fe}''_4\text{Si}_2\text{O}_{17}$.

B. H. B.

New Manganese Ore from Dillenburg. By SCHNEIDER (*Chem. Centr.*, 1888, 1016, from *Zeit. deut. geol. Ges.*, **39**, 829—834).—This ore, which was struck in 1885, is a lode of 0·60—1·0 m. thick.

Its colour varies from light brown to red and dark brown. The crystalline form could not be determined. Hardness 6—7; sp. gr. 3.1026. Analysis gave—

SiO ₂ .	MnO.	CaO.	H ₂ O.	Al ₂ O ₃ .	FeO.	MgO.	Total.
48.92	38.23	8.00	8.49	0.29	0.69	0.28	99.90

It has been named "Inesite."

J. W. L.

Analysis of the Chalybeate Water of Raffanelo in the Commune of Canale Monterano. By F. MANGINI (*Gazzetta*, 17, 517—519).—The spring rises from compact, calcareous rocks interspersed with crystals of calcite, the yield being about 3000 litres per diem. The density at 15° is 0.9745. The water contains 436 c.c. of carbonic anhydride, and the iron, present as ferrous carbonate, is equal to 0.0220 gram per litre; it contains neither nitrates nor nitrites. The solid residue per litre dried at 110° = 1.0915 gram.

The composition of this residue is as follows:—

Carbonic anhydride, CO ₂	0.4240
Silica, SiO ₂	0.0279
Sulphuric acid, H ₂ SO ₄	0.0820
Phosphoric acid, H ₃ PO ₄	0.0014
Chlorine, Cl	0.0053
Iodine	traces
Ferrous oxide, FeO	0.0089
Calcium oxide, CaO	0.3348
Magnesium oxide, MgO	0.0148
Aluminium oxide, Al ₂ O ₃	0.1350
Potassium oxide, K ₂ O	0.0369
Sodium oxide, Na ₂ O	0.0100
Loss	0.0110

C. E. G.

Water of the Nile. By A. MUNTZ (*Compt. rend.*, 107, 231—234). Estimations of the quantity of nitrates in the water of the Nile gave the following results, which are expressed in milligrams per litre:—

	July, 1887.	August, 1887.	September, 1887.
Nitric acid	4.09	4.02	1.83
Equivalent to—			
Potassium nitrate	7.62	7.51	3.71
Or nitrogen	1.067	1.052	0.519

It is evident that the quantity of nitrates is very variable and does not exceed that found in many ordinary rivers. The nitrates are derived partly from the atmosphere and partly from the soil. In tropical districts, the proportion of nitric acid in the rain-water is much more considerable than in temperate climates. The fertility of the district watered by the Nile cannot be attributed to the nitrates contained in the water, but in all probability is due to the constituents of the fine mud which the water deposits.

C. H. B.

Organic Chemistry.

Ethyl Fluoride. By H. MOISSAN (*Compt. rend.*, **107**, 260—263).—Ethyl iodide is allowed to drop gradually on to silver fluoride in a brass vessel, care being taken that the temperature does not rise too high. Any volatilised ethyl iodide is condensed by means of a serpentine lead tube cooled to -20° , and is allowed to fall back upon the silver salt. The last traces of the iodide are removed from the gas by passing it through two U-tubes containing silver fluoride. It is then collected in carefully dried glass vessels over mercury. Ethyl iodide in contact with excess of silver fluoride develops heat, and a gas is evolved, whilst at the same time the yellow colour of the fluoride changes to maroon. Under these conditions, a silver fluoride is formed, and this in contact with a fresh quantity of ethyl iodide at 100° yields silver iodide and ethyl fluoride.

Ethyl fluoride is a colourless gas with an agreeable ethereal odour; sp. gr. 1.70. It liquefies at -48° under normal pressure or under 8 atmos. at 19° , and can be solidified by suddenly diminishing the pressure. It dissolves readily in several liquids. Water dissolves 1.98 vols. at 14° ; ethyl iodide dissolves 14.8 vols.; ethyl bromide, ether, and absolute alcohol especially, also dissolve large quantities. When the liquids are heated, the gas is completely expelled unaltered. Concentrated sulphuric acid also dissolves the gas.

Ethyl fluoride burns with a blue flame which in presence of small quantities of methyl or ethyl chlorides becomes green. Admixture with a small quantity of oxygen produces a bright flame, and with an excess of oxygen the gas explodes violently when ignited. When heated in sealed tubes at 100° with very dilute potash, ethyl fluoride is completely decomposed, and yields potassium fluoride, alcohol, and a large proportion of ether.

Chlorine has no action on ethyl fluoride in the dark after several hours, but gaseous fluorine completely and rapidly decomposes ethyl chloride. It follows that fluorine displaces chlorine from organic as well as inorganic compounds. C. H. B.

Propylene Iodide from Allyl Iodide and Hydrogen Iodide. By H. MALBOT (*Compt. rend.*, **107**, 113—115).—If allyl iodide, cooled at -18° , is treated with a regular current of hydrogen iodide, it yields propylene iodide; but before combination is complete, the latter changes into isopropyl iodide without evolution of propylene. The change takes place slowly, but if the liquid is treated with a further quantity of hydrogen iodide, the change becomes complete.

If the allyl iodide is not cooled, the propylene iodide may decompose very violently: if it is heated, the propylene iodide decomposes as fast as it is formed. When the allyl iodide is mixed with isopropyl iodide, the decomposition of the propylene iodide takes place less rapidly, but still with considerable violence. This constitutes a convenient method for the preparation of propylene. If allyl iodide

is saturated with hydrogen iodide and heated in sealed tubes at 100° , it is completely converted into isopropyl iodide.

In the preparation of isopropyl iodide by Markownikoff's method, if only 10 per cent. of water is added to the glycerol, a very violent reaction takes place, even with red phosphorus, and propylene iodide is formed in large quantity. The formation of propylene iodide cannot be avoided by using anhydrous glycerol, since some water is formed in the reaction.

C. H. B.

Chemistry of Combustion. By C. LÜDEKING (*Annalen*, **247**, 122—128).—The author finds that the characteristic red compound of titanium cyanide and nitride, $3\text{Ti}_3\text{N}_2 + \text{Ti}(\text{CN})_2$, is invariably formed when a small quantity of titanous acid and sodium carbonate contained on a loop of a platinum wire is introduced into the flame of a candle or of a spirit-, petroleum-, or paraffin-lamp. The cyanogen formed by burning 50 litres of methane in air free from ammonia can be detected by means of the prussian-blue reaction. Hence it appears that nitrogen unites directly with carbon at the temperature of the flame of an ordinary candle or spirit-lamp.

W. C. W.

Influence of Temperature on the Production of Higher Alcohols by Fermentation. By L. LINDET (*Compt. rend.*, **107**, 182—183).—Worts prepared by the action of malt on maize and rye were fermented at different temperatures by equal quantities of the same mixture of high and low yeast, the access of air to the liquids being prevented. The alcohols were separated and analysed, and the following table gives the quantities obtained from 30 litres of wort:—

Temperature.	Crude alcohol.	Higher alcohols.	
		Total.	per cent.
32—35°	675 c.c.	3.9	0.58
25—27	1607 „	9.6	0.59
19—21	1834 „	9.9	0.54
8—10	1877 „	9.7	0.52

It is evident that although the differences are greater than can be fairly attributed to experimental error, the proportion of the higher alcohols is not greatly reduced when fermentation takes place at a low temperature.

C. H. B.

Fusel Oil in Beer. By W. M. HAMLET (*Chem. News*, **58**, 81—83, 87—88).—Fusel oil to the extent of from a quarter to one grain per gallon has been found in beer in Sydney, N.S.W., by the following method of analysis. A gallon of beer is shaken by instalments with chloroform, 50 c.c. being used for the first half gallon, another 50 c.c. is added and used with the next pint, finally 50 c.c. more is added, making in all 150 c.c. of chloroform, and the rest of the gallon of beer extracted. The extract is washed with water to remove ethyl alcohol and any valeral from the hops, it is then heated under pressure for six hours at 85° , with 5 grams of potassium dichromate and 2 grams of concentrated sulphuric acid, finally it is distilled; the residue mixed

with water and distillation continued. The distillate has a strong odour of valeric acid; it is boiled with barium carbonate, the chloroform distilled off, and the quantity of barium valerate determined and attributed to fusel oil. If the chloroform extract washed with water does not yield valeric acid, whilst the unwashed chloroform extract does, the author accepts it as an indication that hops have been employed, the valeric acid originating in the latter case from the valeral of the hop oil.

D. A. L.

Oxidation of Glycerol. By E. FISCHER and J. TAFEL (*Ber.*, **21**, 2634—2637. Compare this vol., p. 358).—Almost pure glycerose can be prepared by treating lead glyceroxide with dry bromine, but the success of the experiment depends greatly on the state of aggregation of the glyceroxide. Lead glyceroxide is prepared as follows: dry finely-divided lead hydroxide (500 grams) is added to boiling, aqueous glycerol (1000 grams), containing about 85 per cent. of glycerol, the mixture stirred until it becomes homogeneous, cooled quickly in ice-cold water with constant stirring, and finally $2\frac{1}{2}$ litres of ice-cold alcohol added. The glyceroxide is washed by shaking with alcohol and ether and dried at 100° . The yield is 85 per cent. of the hydroxide employed, and the product contains small quantities of nitric acid. It explodes when heated, and takes fire when placed in contact with chlorine or bromine. (Compare Morawski, *Abstr.*, 1880, 428.)

For the preparation of glycerose, the lead glyceroxide is spread in thin layers and kept under a bell-jar, in proximity to half its weight of bromine contained in a shallow dish, until the bromine is entirely absorbed. The product is extracted with alcohol, the solution quickly concentrated on the water-bath in a partial vacuum, and mixed with barium carbonate to remove free acid. On shaking with ether, the greater part of the glycerose passes into solution, and the remainder can be obtained from the residue by extracting with warm alcohol, precipitating with ether, and repeating the operation. The ether is evaporated from the combined extracts, water added and the solution concentrated on the water-bath in a partial vacuum.

The syrup thus obtained contains traces only of inorganic matter and is free from glycerol and acids. The reducing power of a syrup prepared from 860 grams of the glyceroxide is equal to that of a solution containing 55 grams of grape-sugar, but the reducing power is greatly diminished when the syrup is evaporated to dryness, probably owing to polymerisation. The diluted syrup ferments with yeast, and when warmed with phenylhydrazine, phenylglycerosazone is precipitated. It yields two hydroxy-acids when warmed with concentrated hydrocyanic acid, showing that glycerose is a mixture. These acids, which can be separated by means of their barium salts, are probably erythroglicic acid and *trihydroxyisobutyric* acid.

F. S. K.

Polybasic Glyceroxides. By DE FORCRAND (*Compt. rend.*, **107**, 269—272).—The heat of neutralisation of glycerol by three successive equivalents of sodium hydroxide at 20° develops +0.50, +0.14 and +0.04 Cal. respectively. The corresponding values in the case of potassium hydroxide being +0.56, +0.14, +0.09.

When monopotassium glyceroxide methylate, $C_3H_7O_3K + MeOH$, is mixed with an equivalent quantity of potassium methoxide dissolved in methyl alcohol, the liquid evaporated to dryness, and the residue heated in an atmosphere of hydrogen for several hours at 180° , the product is not dipotassium glyceroxide, but a compound of monopotassium glyceroxide with the methoxide, analogous to the sodium compound previously obtained under similar conditions. It would seem that the combination of an alkaline monoglyceroxide with the corresponding alkyl oxide is a general reaction.

Attempts to prepare trisodium glyceroxide in a similar manner were equally fruitless.

C. H. B.

Action of Ammonia on Epichlorhydrin. By A. FAUCONNIER (*Compt. rend.*, **107**, 115—117).—When a current of ammonia gas is passed through epichlorhydrin at the ordinary temperature there is no appreciable action, but if the two are left in contact for some time, the gas is slowly absorbed and the liquid gradually becomes viscous. Towards the close of the reaction, a considerable quantity of heat is developed, and it is necessary to cool the liquid in order to prevent carbonisation. When elevation of temperature is prevented, the liquid is converted into a white mass of microscopic, truncated octahedra. These are washed with cold alcohol, dissolved in dilute acetic acid, and the liquid neutralised with ammonia, when the crystals separate in their original form. They consist of *tri-chlorhydroxypropylamine*, $N(C_2H_4Cl \cdot OH)_3$, melt at $92-93^\circ$, are almost insoluble in cold neutral solvents, and dissolve readily in dilute acids, forming non-crystallisable salts from which the base is precipitated by ammonia. The base alters readily, and if dissolved in hot water or alcohol is converted into a non-crystallisable syrup. The hydrochloride crystallises in needles which melt without alteration at 173° , and are only slightly soluble in alcohol, but somewhat soluble in water. With sodium phosphotungstate, an acetic acid solution of the base yields an amorphous white precipitate; with the phosphomolybdate, an amorphous, lemon-yellow precipitate; with Nessler's reagent, a white amorphous, precipitate; with Bouchardat's reagent, a pale-brown precipitate; but no precipitate with potassium mercuriodide, potassium cadmioidide, auric chloride, platinic chloride, mercuric chloride, potassium ferrocyanide, or picric acid. If the alcoholic solution is mixed with silver nitrate, it yields a precipitate of silver chloride in the cold; ammoniacal silver nitrate is slowly reduced in the cold with formation of a mirror.

The action of alkalis on trichlorhydroxypropylamine at the ordinary or a higher temperature converts it into a substance which closely resembles gelatin, and is insoluble in all ordinary reagents and even in boiling concentrated acids.

C. H. B.

Mannitol Dibenzoate. By J. MEUNIER (*Compt. rend.*, **107**, 346—348).—If a solution of mannitol, dehydrated in the manner previously described (this vol., p. 950) and containing a considerable quantity of alcohol not converted into ethyl chloride, is mixed with benzoic chloride, there is considerable development of heat; hydrogen

chloride is evolved and ethyl benzoate is formed. After treatment with alkali to remove zinc, the benzoic chloride is distilled and deposits transparent, monoclinic or triclinic crystals of mannide dibenzoate, $C_{30}H_{22}O_6$, which is very slightly soluble in water or in cold alcohol, but dissolves in boiling alcohol, from which it separates in long prisms melting at 132° . It is soluble in chloroform, glacial acetic acid, sulphuric acid, and benzene. It is not decomposed by dilute or concentrated sulphuric acid, nor by aqueous potash, but is attacked by boiling alcoholic potash, with formation of benzoic acid and some other substance, but no appreciable quantity of mannitol.

In order to avoid the formation of ethyl benzoate in the preparation of this compound, care should be taken that the alcohol is as far as possible converted into ethyl chloride before benzoic chloride is added. After any ethyl benzoate that may have been formed has been expelled by evaporation, the product is washed with cold alcohol to remove a gummy substance, and crystallised from boiling alcohol.

C. H. B.

Levulose. By E. JUNGFLEISCH and L. GRIMBERT (*Compt. rend.*, 107, 390—393).—Experiments on the inversion of cane-sugar, which will be described in a subsequent paper, confirm the older results, and are at variance with Herzfeld and Winter's statement that saccharose yields 2 mols. of levulose and 1 mol. of glucose.

The levulose employed was purified by crystallisation from alcohol. The rotatory power of a freshly prepared aqueous solution gradually diminishes, but the change is not so strongly marked as in the case of glucose, although, as in that case, it is accelerated by heating. Prolonged heating at temperatures up to 100° causes a reduction in the rotatory power, and concordant results can only be obtained below 40° . The rotatory power of pure levulose varies inversely as the temperature, and increases with the concentration of the solution. The equation $[\alpha]_D = -101.38 - 0.56t + 0.108(p - 10)$, where t is the temperature, and p the weight of levulose in 100 c.c., holds good between 0° and 40° , and for all concentrations up to 100° . The rotatory power of pure levulose differs from that calculated from the rotatory power of invert sugar on the assumption that the latter is a mixture of levulose and glucose in equivalent proportions.

C. H. B.

Carbohydrates. By M. HÖNIG and L. JESSER (*Monatsh.*, 9, 562—578; compare this vol., p. 246).—The authors have prepared crystallised anhydrous levulose by repeatedly crystallising the pure hydrated substance having the formula $2C_6H_{12}O_6 + H_2O$ from absolute alcohol. At 17.5° it has a sp. gr. = 1.6691. Its specific rotatory power is -113.963 at 20° , and varies both with the concentration of the solution and the temperature. The change in rotatory power owing to variation in the concentration of the solution is represented when $t = 20^\circ$ by the expression—

$$[\alpha]_D^{20} = -113.9635 + 0.25831q,$$

that due to variation in temperature, by $[\alpha]_D^t = -a + 0.67142t$. The reducing power of levulose for all states of concentration less than

1 per cent. is smaller than that of dextrose. The amount of reduced copper, y , obtainable from a particular quantity of the sugar, x , can be calculated by means of the equation—

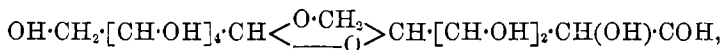
$$y = -5.372 + 1.91856x - 0.0007605x^2.$$

G. T. M.

Compounds of Phenylhydrazine with Sugars. By E. FISCHER (*Ber.*, **21**, 2631—2634; compare this vol., pp. 39 and 934).—The osazones of all saccharoses dissolve in cold, fuming hydrochloric acid with a dark-red coloration, and the osazone-group, $N_2HPh:\dot{C}:\dot{C}:N_2HPh$, is thereby converted into the group $\cdot CO \cdot CO \cdot$.

Oxyglucose, $OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot CO \cdot COH$, is obtained when phenylglucosazone is mixed with 10 times its weight of ice-cold, fuming hydrochloric acid. The osazone dissolves, and in a short time phenylhydrazine hydrochloride separates; at 5° to 10° , the reaction is at an end in about an hour and a half. The solution is quickly filtered through glass-wool, the residue washed with a small quantity of concentrated hydrochloric acid, the filtrate diluted with ice-cold water, neutralised with lead carbonate, and filtered. The filtrate is warmed with animal charcoal, mixed with excess of baryta-water, and the precipitated lead compound of oxyglucose decomposed with dilute sulphuric acid. After removing the excess of acid, and evaporating in a partial vacuum, the product is obtained in the form of a syrup. The yield is about 30 per cent. of the theoretical quantity. Oxyglucose reduces Fehling's solution on boiling, is precipitated by concentrated baryta-water or a solution of basic lead acetate, and does not ferment with yeast. When an aqueous solution is mixed in the cold with phenylhydrazine acetate, phenylglucosazone separates in a few minutes, but when the mixture is heated at 50 — 60° the reaction is completed in a very short time, and the osazone obtained is almost pure.

Oxylactose was prepared in like manner from phenyllactosazone, but was not isolated. When the aqueous solution is treated with phenylhydrazine acetate in the cold, phenyllactosazone separates in from 5 to 10 minutes; at 60° to 70° , the formation of the osazone is rapid and complete, and on cooling it crystallises from the solution. Oxyglucose and galactose are formed when the aqueous solution of oxylactose is warmed with hydrochloric acid. From this fact, the author concludes that the constitution of milk-sugar is probably—



but he does not exclude the alternative possibility, namely, that the two central carbinol-groups (in brackets) take part in the anhydride formation. In accordance with this view, milk-sugar should yield on oxidation an acid, $C_{12}H_{22}O_{13}$, and it was found that when it is treated with bromine in cold aqueous solution a syrupy acid is, in fact, formed. Maltose has probably an analogous constitution.

F. S. K.

Vinylamine and Bromethylamine. By S. GABRIEL (*Ber.*, **21**, 2664—2669).—Vinylamine (this vol., p. 668) is best prepared by

treating a cold solution of bromethylamine hydrobromide (1 mol.) with potash (1 mol.), keeping the mixture at 45—48° for 10 minutes in a closed flask, saturating with alkali, and distilling. The last portions of the distillate contain a less volatile base, the *picrate* of which, $C_4H_{12}N_2O, 2C_6H_3N_3O_7$, crystallises in yellow needles, melts at 205—206°, and is sparingly soluble in water. For this reason, the distillate should be collected separately as soon as a small portion gives a precipitate with a 1 per cent. solution of picric acid.

This method of preparation depends on the fact that at 45—48° bromethylamine undergoes molecular change into vinylamine hydrobromide.

Hydroxyethylamine nitrate, $OH \cdot CH_2 \cdot CH_2 \cdot NH_2, HNO_3$, is obtained when bromethylamine nitrate, prepared by mixing equivalent quantities of silver nitrate and bromethylamine hydrobromide in aqueous solution, is boiled with silver nitrate; also, when vinylamine is evaporated with excess of nitric acid. It forms flat, colourless hygroscopic crystals, melts at 52—55°, and explodes on further heating. With sodium picrate, a concentrated aqueous solution gives the salt already described (this vol., p. 440).

When a hot, dilute solution of silver sulphate is mixed with a little less than the molecular proportion of bromethylamine hydrobromide, half the bromine is precipitated as silver bromide, and after boiling for several hours the remainder of the bromine separates as silver bromide when the solution is evaporated. Amidoethylsulphuric acid (*loc. cit.*) is obtained when the solution is freed from silver and concentrated. The constitution of this compound is probably $CH_2 < \begin{smallmatrix} CH_2 \cdot O \\ NH_3 \cdot O \end{smallmatrix} > SO_2$.

Vinylamine combines with sulphurous anhydride with formation of taurine.

Freshly prepared vinylamine hydrochloride in doses of 0.03 gram to every kilo. of body-weight proved fatal to guinea-pigs within 10 hours, and doses of 0.015 gram within 24 hours. F. S. K.

Hexamethylenetetramine. By P. GRIESS and G. HARROW (*Ber.*, 21, 2737—2739).—*Dinitrosopentamethylenetetramine*, $C_6H_{10}N_4(NO)_2$, is obtained when a solution of sodium nitrite is gradually added to a well-cooled aqueous solution of hexamethylenetetramine containing a slight excess of nitric acid. It crystallises from boiling alcohol, in which it is rather easily soluble, in thick, indented, slightly yellow needles, and from chloroform, in which it is more sparingly soluble, in short, well-defined prisms melting at 207° with decomposition. It has a neutral reaction and a bitter taste, and is almost insoluble in ether and cold alcohol, but dissolves in boiling water with considerable decomposition. In alcoholic alkaline solutions, it is very stable towards reducing agents, but when boiled for a few minutes with very dilute hydrochloric acid it is decomposed, quantitatively and completely, into formaldehyde, ammonia, and nitrogen.

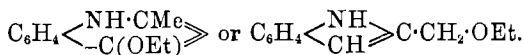
F. S. K.

Ethylenimine. By A. LADENBURG and J. ABEL (*Ber.*, 21, 2706—2707).—The authors have prepared diethylenediamine by treating ethylene chloride with ethylenediamine, and the experiments which

have hitherto been made seem to show that this diamine is not identical with ethylenimine (this vol., p. 441). F. S. K.

Thiazole. By A. HANTZSCH and G. POPP (*Ber.*, **21**, 2582—2583).—*Thiazole*, $N \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{CH} \cdot \text{S} \end{smallmatrix}$, is obtained by boiling the product of the action of nitrous acid on the amidothiazole (formed by the condensation of thiocarbamide and dichlorether) with alcohol. It has an odour similar to that of pyridine, but its salts are distinct from those of that base. N. H. M.

Action of Sodium on Ethyl Chloracetate. By R. FITTIG and A. ERLÉNACH (*Ber.*, **21**, 2647—2650).—The compound described as acetoisopropyl alcohol (this vol., p. 1052) is acetol ethyl ether (Henry, *Compt. rend.*, **93**, 421). It yields acetone and ethyl alcohol when treated at 0° with sodium amalgam and dilute hydrochloric acid, and reduces copper acetate in the cold. The *hydrazide*, $C_{11}H_{16}N_2O$, boils at 165°, and when heated at 80—90° with an aqueous alcoholic solution of sodium acetate and sodium chloride, containing a few drops of acetic acid, it yields a colourless, crystalline compound $C_{11}H_{13}NO$, melting at 142·5°, which is probably ethoxymethylindole,



F. S. K.

Hydrolysis of Fat. By R. BENEDIKT (*Monatsh.*, **9**, 518—520; compare *Abstr.*, 1884, 946; 1885, 313 and 315; 1887, 620 and 914; and this vol., pp. 578 and 815).—The author finds that the acid obtained by the hydrolysis of fat with sulphuric acid and subsequent distillation with superheated steam, contains neither hydroxystearic nor oleic acid, but an unsaturated acid, in all probability isoleic. Commercial stearic acid obtained from fat in the above-mentioned way, is to be regarded as a mixture of stearic, palmitic, and isoleic acids.

G. T. M.

Drying Oils. By A. BAUER and K. HAZURA (*Monatsh.*, **9**, 459—468; compare *Abstr.*, 1887, 359, 798, 913, and this vol., pp. 816, 817).—In this paper, the authors contest many of the views advanced by Mulder on the products of oxidation of drying oils. They find that the rate of oxidation, and consequent hardening, of drying oils, depends on the ratio in which linoleic and linolenic acids are present; the more linolenic acid there is in the oil, the more rapid is the oxidation, which consists not only in the satisfying of the uncombined valencies with oxygen, but also in the formation of products containing hydroxyl-groups. On oxidation, the salts of the acids behave in a precisely similar manner.

When thin layers of drying acids are left exposed to the air for a considerable period at ordinary temperatures, or for a shorter time at 80°, the product is an anhydride insoluble in ether, but furnishing soluble acids when heated with alkalis. The drying of oils depends on the presence of linoleic, linolenic, and isolinolenic acids, and in no way on that of oleic acid, which forms no solid oxidation-products on exposure to air.

G. T. M.

Oxidation of Unsaturated Fatty Acids by Permanganate.

By K. HAZURA (*Monatsh.*, **9**, 469—474).—The author confirms the opinions advanced by Saytzeff (*Abstr.*, 1886, 140) as to the action of permanganate on unsaturated fatty acids. Experiments with the unsaturated acids obtained from poppy-seed oil show that practically no hydroxy-derivatives of fatty acids are formed when permanganate is added to a solution of potassium salts of the acids containing an amount of sulphuric acid just sufficient to neutralise the alkali liberated from the permanganate. On the other hand, when the precaution of adding the sulphuric acid is neglected, the alkali set free on the reduction of the permanganate rapidly brings about the formation of hydroxy-derivatives, a result which is considerably hastened by the addition of free potash. G. T. M.

Acids from Drying Oils. By K. HAZURA and A. GRÜSSNER (*Monatsh.*, **9**, 475—484; compare *Abstr.*, 1887, 359, 798, 913, and this vol., pp. 816, 817).—When alkaline solutions of the liquid, fatty acids of castor oil are oxidised with permanganate, *trihydroxystearic acid*, crystallising in microscopic needles melting at 140—142°, and its isomeride, *isotrihydroxystearic acid*, also forming minute needles and melting at 110—111°, are formed, in the ratio of one of the former to two of the latter, together with lower members of the series of fatty acids. Since no dihydroxystearic acid results from the oxidation, no olein can be present in castor oil. This is the only observed case in which that constituent is absent in a drying oil. The authors suggest the name *ricinolic acid* for trihydroxystearic acid, and *ricinisolic acid* for its isomeride. G. T. M.

Ricinoleic Acid. By F. KRAFFT (*Ber.*, **21**, 2730—2737).—Pure ricinoleic acid can be prepared as follows:—Castor oil is hydrolysed with concentrated potash, the salt completely decomposed by heating for as short a time as possible with concentrated hydrochloric acid, and the liquid acid, after washing with water, cooled until it solidifies. It is then freed from oily impurities by pressure at a gradually increasing temperature. It is a hard, white, crystalline substance, melts at 16—17°, and solidifies again when cooled considerably below its melting point. The solid acid seems to undergo no change when exposed to the air for several weeks, but in the liquid state it alters slightly. It commences to boil at about 250° (15 mm.), and an oily liquid distils, the temperature rising considerably, but *œnanthol* and *undecylenic acid* are not formed. A compound, $C_{18}H_{33}O_2$, boiling at about 230° (15 mm.) is obtained when the distillate is fractionated at 15 mm. pressure. Barium ricinoleate is readily soluble in hot, but only sparingly in cold water. Castor oil which has been kept for a long time in a cool place deposits considerable quantities (3 to 4 per cent.) of a granular, crystalline substance which contains the glycerides of stearic and ricinoleic acids.

The constitution of ricinoleic acid is probably



$CH_3 \cdot [CH_2]_5 \cdot CO \cdot [CH_2]_{10} \cdot COOH$; in accordance with this view, the

author found that normal heptylic acid is formed, together with azelaic and oxalic acids, when ricinoleic acid is oxidised with nitric acid.

Ricinelaïdic acid boils at about 250° (15 mm.) with partial decomposition, and yields normal heptylic acid when treated with nitric acid.

Ricinic acid, $C_{18}H_{34}O_3$, is formed when barium ricinoleate is heated in a partial vacuum; methyl hexyl ketone distils and the acid in the residual salt is precipitated with hydrochloric acid and purified by distillation. It crystallises from alcohol in plates, melts at about 81° , and boils at about 250 — 252° (15 mm.) with slight decomposition. When treated with nitric acid, it yields principally normal heptylic acid and an acid melting at 100 — 107° . Towards bromine and potash, it behaves like ricinoleic and ricinelaïdic acid. F. S. K.

Tetramethylene-derivatives. By M. FREUND and E. GUDEMAN (*Ber.*, 21, 2692—2699).—*Tetramethylenecarboxylamide*, $C_4H_7\cdot CO\cdot NH_2$, is obtained by heating ammonium tetramethylenecarboxylate at 230 — 250° and distilling the product. It crystallises from alcohol in plates, melts at 138° , sublimes unchanged, and is readily soluble in water, ether, chloroform, and benzene. Attempts to convert the amide into the corresponding amine by means of bromine and alkalis were unsuccessful, as were also similar experiments made with the object of preparing carbamide-derivatives. The *nitrile*, $C_4H_7\cdot CN$, prepared by heating the amide with phosphoric anhydride and fractionating the product, is a colourless, agreeably smelling liquid boiling at 150° . It is converted into the acid when heated with potash. The ethyl salt, prepared by saturating an alcoholic solution of the acid with hydrogen chloride, boils at 159 — 162° (compare Perkin, this Journ., 1887, 12). The *chloride*, $C_4H_7\cdot COCl$, obtained by boiling the acid with phosphorous chloride, is a fuming liquid boiling at 142 — 143° . The *anhydride*, $(C_4H_7\cdot CO)_2O$, prepared by distilling a mixture of the chloride and the sodium salt, boils at 160° .

Tetramethylenecarbanilide, $C_4H_7\cdot CO\cdot NHPh$, is formed when the amide is boiled with aniline. It crystallises from alcohol in long, pointed needles, melts at 111° and is sparingly soluble in hot, and insoluble in cold water.

Tetramethylenemethylamine (tetramethylenylamine) hydrochloride, $C_4H_7\cdot CH_2\cdot NH_2\cdot HCl$, is prepared by reducing the nitrite with sodium and absolute alcohol, distilling the reaction-product with steam, collecting the distillate in hydrochloric acid, evaporating the solution to dryness, and extracting the residue with alcohol to remove traces of ammonium chloride. It crystallises from alcoholic ether, melts at 234 — 236° with decomposition, and is readily soluble in water and alcohol, but insoluble in ether. The *platinochloride*, $(C_4H_9N)_2\cdot H_2PtCl_6$, is crystalline. The free base is an oil boiling at 82 — 83° ; it has a strongly basic odour, an alkaline reaction, and absorbs carbonic anhydride from the air.

Tetramethylenylcarbamide, $C_4H_7\cdot CH_2\cdot NH\cdot CO\cdot NH_2$, prepared by evaporating a solution of the hydrochloride of the amine with potassium cyanate, crystallises from hot alcohol in long, scaly needles, melts

at 116°, and is readily soluble in hot, but only sparingly in cold water.

Tetramethylenylthiocarbamide, $C_4H_7 \cdot CH_2 \cdot NH \cdot CS \cdot NH_2$, prepared by boiling the hydrochloride of the amine with ammonium thiocyanate, crystallises from water or alcohol in slender needles and melts at 67—68°. F. S. K.

Tetric Acid and its Homologues. By R. MOSCHELES and H. CORNELIUS (*Ber.*, **21**, 2603—2609).—*Ethyl tetratate*, $C_7H_{10}O_8$, forms lustrous crystals, melts at 30°, and boils at 180° under 70 mm. pressure. It dissolves in boiling aqueous soda, and is precipitated unchanged by dilute sulphuric acid. The ethyl salts of pentic and phenyltetric acids are oils. None of these salts have any analogy with ethyl succinosuccinate: they are colourless, dissolve sparingly in water, readily in alcohol and ether; the solutions show no fluorescence; they are readily hydrolysed by hydrogen chloride and bromide, but not by alkalis. It is therefore improbable that tetric acid and its homologues are alkylated succinosuccinic acids (Wedel, *Annalen*, **219**, 106). The formation of tetric acid from ethyl bromomethylacetoacetate is best explained by the formula $\langle \begin{smallmatrix} CHMe \cdot CO \\ CO \cdot CH_2 \end{smallmatrix} \rangle O$ (Michael, *J. pr. Chem.* [2], **37**, 503).

It is probable that in the formation of alkyl salts an intramolecular migration takes place, the group $\equiv CH \cdot CO \equiv$ becoming $\equiv C : C(OH) \equiv$, as the salts do not react with phenylhydrazine, whilst the acids do.

Pentic acid phenylhydrazide, $C_6H_5O_2 \cdot N_2HPh$, prepared by dissolving pentic acid (1 mol.) and phenylhydrazine (1 mol.) in 50 per cent. acetic acid, is crystalline.

Tetrinamide, $C_6H_7NO_2$, obtained by heating the acid with alcoholic ammonia at 150°, melts at 212°.

Bromotetric acid, $C_5H_5O_3Br$, forms white crystals melting at 75°.

Phenyltetric acid, $C_{11}H_{10}O_8$, is prepared by heating ethyl bromobenzylacetoacetate in a water-bath. It is sparingly soluble in hot water, and is much more stable than the other acids of the group. The *benzoyl-derivative*, $C_{18}H_{14}O_4$, crystallises from alcohol in needles melting at 110°. N. H. M.

Constitution of Mesitonic Acid. By R. ANSCHÜTZ and C. GILLET (*Annalen*, **247**, 99—111).—The authors regard mesitonic acid as α -dimethyllevulinic acid, as it closely resembles levulinic acid in its behaviour with certain reagents. A crystalline compound is deposited when phenylhydrazine acetate is added to an aqueous solution of mesitonic acid. The compound melts at 121.5° and forms prismatic crystals soluble in benzene and alcohol. It is very unstable and is decomposed by boiling with hydrochloric acid, yielding the compound $CMe_2 \langle \begin{smallmatrix} CH_2 \cdot CMe \\ CO \cdot NPh \end{smallmatrix} \rangle N$. Mesitonic acid yields dimethylmalonic acid when oxidised with nitric acid, and α -dimethylvalerolactone when reduced with a large excess of sodium amalgam.

α -Dimethylvalerolactone is crystalline, melts at 52°, and boils at 86° under 15 mm. pressure. In the formation of dimethyllevulinic acid from mesityl oxide, $CMe_2 \cdot CH \cdot COMe$, a hydrochloric acid additive pro-

duct, $\text{CMe}_2\text{Cl}\cdot\text{CH}_2\cdot\text{COMe}$, is first formed; this is converted into the nitrile of α -dimethyllevulinic acid, $\text{CN}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{COMe}$, by the action of potassium cyanide, and on saponification the amide and the free acid are produced.

W. C. W.

Ethyl Oxallevalinate. By W. WISLICENUS (*Ber.*, **21**, 2583—2586).—*Ethyl oxallevalinate*, $\text{C}_{11}\text{H}_{18}\text{O}_6$, is prepared by adding rather more than 1 mol. of ethyl oxalate to sodium ethoxide previously treated with 10 parts of absolute ether; after 12 hours, the calculated amount of ethyl levulinate is added. The whole is left for some days, cooled and shaken with water; the aqueous solution is separated from the ether, and made acid, when the ethyl oxallevalinate separates as a light oil. It is purified by means of the copper or potassium compound and can then be distilled. It is a thick, colourless oil, boils at 198° under 27 mm. pressure, is insoluble in water, readily soluble in alcohol and ether. The alcoholic solution gives an intense red colour with ferric chloride. The *copper compound*, $(\text{C}_{11}\text{H}_{15}\text{O}_5)_2\text{Cu}$, crystallises from much boiling absolute alcohol in very small, dark green needles which melt with decomposition at 190 — 200° . It is insoluble in water. The *potassium compound* crystallises in hair-like, matted, lustrous needles, melts at 180 — 183° with evolution of gas, and is very readily soluble in water.

When ethyl oxallevalinate is heated with phenylhydrazine on a water-bath, the compound $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}$ is obtained. This crystallises in groups of lustrous needles, melts at 83 — 84° , and is readily soluble in ether, benzene, and hot alcohol. It is a feeble base, and dissolves in strong hydrochloric acid, but is precipitated on diluting. When boiled with alcoholic potash, the potassium salt of the acid $\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_2$ is formed. The *free acid* crystallises in needles with 1 mol. H_2O , melts at 165 — 167° , and dissolves readily in alcohol and in aqueous sodium carbonate.

N. H. M.

Pimelic Acid from Menthol. By G. ARTH (*Compt. rend.*, **107**, 107—110).—The acid, $\text{C}_7\text{H}_{12}\text{O}_4$, produced by the oxidation of menthol (*Ann. Chim. Phys.* [6], **7**, 439), is not identical with normal propylsuccinic acid prepared by Waltz's method. The amide of the former is much more soluble in water and crystallises in prismatic crystals melting at 191° . The amide of the latter separates in small, hard crystals or in opaque, dendritic groups.

C. H. B.

Determination of the Molecular Weight of Dimethyl Diacetyl-racemate by Raoult's Method. By R. ANSCHÜTZ (*Annalen*, **247**, 111—122).—Dimethyl diacetyl-racemate is formed when a benzene solution of the dimethyl salts of the dextro- and lævo-gyrate diacetyl-tartaric acids evaporate spontaneously. The crystals melt at 86° , and are identical in every respect with the compound obtained by boiling dimethyl-racemate with acetic chloride.

Determinations of the molecular weight by Raoult's method gave unexpected results. The molecular weight for dimethyl diacetyldextro-tartrate and of dimethyl diacetyl-racemate are identical, whilst it

was to be expected that the latter would have had a molecular weight double that of the former. W. C. W.

Water of Crystallisation of certain Pyrotritartrates. By C. BÖTTINGER (*Annalen*, **274**, 255—256).—In a former paper, the author stated that the barium and calcium salts of pyrotritartronic acid are deposited from dilute solutions with 5 and 6 mols. H_2O respectively:— $(\text{C}_7\text{H}_7\text{O}_3)_2\text{Ba} + 5\text{H}_2\text{O}$ and $(\text{C}_7\text{H}_7\text{O}_3)_2\text{Ca} + 6\text{H}_2\text{O}$. From concentrated solutions, the salts crystallise with 4 mols. H_2O , e.g., $(\text{C}_7\text{H}_7\text{O}_3)_2\text{Ba} + 4\text{H}_2\text{O}$. W. C. W.

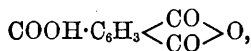
Action of Ethereal Salts of Diazoacetic Acid on Ethereal Salts of Unsaturated Acids. By E. BUCHNER (*Ber.*, **21**, 2637—

2647).—*Methyl fumaricdiazoacetate*, $\left\langle \begin{array}{c} \text{CH}(\text{COOMe})\cdot\text{N} \\ \text{CH}(\text{COOMe})\cdot\text{N} \end{array} \right\rangle \text{CH}\cdot\text{COOMe}$,

is obtained when methyl fumarate (1 mol.) and methyl diazoacetate (1 mol.) are warmed together. The reaction commences at about 60° , and a considerable amount of heat is generated. The product, which was only obtained in an impure condition, is a thick, yellowish oil, and is readily soluble in hot water, but is not miscible with ether in all proportions. It immediately decolorises alkaline potassium permanganate, and dissolves in aqueous or alcoholic potash with a transient, but intense, yellow coloration, forming a colourless *potassium* salt, from which the *acid* was obtained in the form of a yellowish, crystalline mass, melting at 220° with decomposition. The *barium* salt is readily soluble. The methyl salt is decomposed when boiled with mineral acids, yielding carbonic anhydride, the corresponding hydrazine salt, and an acid, probably succinic acid.

Trimethyl 1.2.3-trimethylenetricarboxylate, $\text{C}_9\text{H}_{12}\text{O}_6$, is obtained when the preceding compound is heated; at about 160° , evolution of gas commences, reaching its maximum at about 200° ; on continued heating, a colourless liquid distils, which solidifies to a crystalline mass on cooling. It crystallises from boiling alcohol or water in colourless needles, melts at 61° , boils at 267° (732 mm.), and is readily soluble in alcohol, ether, benzene, and light petroleum. It is not acted on by bromine or by alkaline potassium permanganate.

Trimethylenetricarboxylic acid is obtained when the methyl salt is hydrolysed with alcoholic potash (compare Perkin, *Trans.*, 1885, 801). It crystallises from ether in small, colourless needles, melts at 220° , and is sparingly soluble in ether. The ammonium salt crystallises in plates, and is readily soluble. The *anhydride*,



is formed when the acid is distilled in a partial vacuum. It crystallises from ether in small prisms, melts at $186\text{--}189^\circ$, boils at 265° (75 mm.), is readily soluble in water and alcohol, and moderately soluble in ether. The *lead*, *barium*, and *silver* salts of the anhydride are moderately soluble in water, the *calcium* salt readily.

Ethyl cinnamicdiaoacetate, $\left\langle \begin{array}{c} \text{CHPh} - \text{N} \\ \text{CH}(\text{COOH}) \cdot \text{N} \end{array} \right\rangle \text{CH} \cdot \text{COOEt}$, prepared

by heating a mixture of ethyl diazoacetate and ethyl cinnamate to 110° , and then very gradually to 130° , crystallises from alcohol in colourless prisms, melts at 79° , and is readily soluble in alcohol, ether, benzene, and glacial acetic acid. It dissolves in alkalis with a transient, yellow coloration, is not acted on by cold concentrated sulphuric acid, and is decomposed into nitrogen and ethyl phenyltrimethylenedicarboxylate when heated above its melting point.

Cinnamicdiaoacetic acid, $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_4$, prepared by hydrolysing the ethyl salt with soda, separates from water in almost colourless, nodular crystals, melts at 178° with decomposition, is readily soluble in boiling water, and moderately soluble in alcohol and ether. It is completely decomposed when heated at 130° for some time, but is only slowly acted on by cold, alkaline potassium permanganate. It yields a colourless bromo-derivative, which crystallises from water and melts at 227° with decomposition. When reduced with zinc and glacial acetic acid, it gives an acid which crystallises in needles and is readily soluble in water. The *silver* salt, $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Ag}_2$, is insoluble in water, and when heated at 140° gives a nitrogenous compound; this sublimes in needles, and crystallises from alcohol in plates melting at 228° . The *barium* salt is readily soluble in water.

Ethyl phenyltrimethylenedicarboxylate, $\text{C}_{15}\text{H}_{14}\text{O}_4$, is obtained when ethyl cinnamicdiaoacetate is distilled under diminished pressure. It is a thick oil, boils at $256\text{--}257^\circ$ (120 mm.), and is only slowly oxidised by alkaline potassium permanganate. It is not acted on by bromine in cold acetic acid solution.

Phenyltrimethylenedicarboxylic acid, $\text{C}_{11}\text{H}_8\text{O}_4$, crystallises from alcohol in colourless prisms, melts at 175° , is readily soluble in alcohol and ether, and moderately in water. It is not oxidised by alkaline potassium permanganate. An acid, probably phenyltrimethylenedicarboxylic acid, is obtained when the dicarboxylic acid is distilled under diminished pressure. It separates from ether in colourless crystals, melts at 134° , boils at 282° (190 mm.), and is not oxidised by alkaline potassium permanganate. The *ammonium* salt is crystalline; the *silver* salt is sparingly soluble in water. Ethyl ortho-nitrophenylpropionate combines with ethereal salts of diazoacetic acid, but the author has not hitherto succeeded in isolating the intermediate nitrogenous product.

F. S. K.

Action of Sulphuric Acid on Bromo-derivatives of Benzene. By J. HERZIG (*Monatsh.*, 9, 586—588).—The author has confirmed his earlier experiments (*Abstr.*, 1882, 46), and refuses to accept the explanation of them offered by Jacobsen (this vol., p. 137). In conclusion he points out the very different behaviour of monobromodurene and monobromobenzene towards sulphuric acid, the reaction in the former case being comparatively simple, and admitting of ready explanation, whilst the latter is only attacked with difficulty and at relatively high temperatures, furnishing compounds not nearly so intimately related to bromobenzene.

G. T. M.

Tribromotrinitrobenzene. By C. L. JACKSON and J. F. WING (*Amer. Chem. J.*, **10**, 283—294).—Koerner has stated that he has prepared tribromotrinitrobenzene, but Wurster and Bevan have denied it. The authors, however, have prepared this substance by Koerner's method, and shown that his critics failed by using a nitric acid containing nitrous acid (compare this vol., p. 136).

Tribromotrinitrobenzene, $C_6Br_3(NO_2)_3$.—Symmetrical tribromobenzene is first converted into tribromodinitrobenzene, and this then further nitrated by a mixture of nitric acid of sp. gr. 1.51 and fuming sulphuric acid; the product requires purifying from unaltered material and from tetrabromodinitrobenzene (see below). The yield is from 15 to 20 per cent. of the theoretical. It crystallises well from chloroform or benzene, is almost insoluble in alcohol, and melts at 285° (uncorr.). It reacts readily with a number of substances, but few of the products have been investigated. When treated with alcoholic ammonia, a pale-yellow, amorphous substance separates, namely, *triamidotrinitrobenzene*, $C_6(NH_2)_3(NO_2)_3$. It is insoluble in ordinary reagents, but may be crystallised from aniline or nitrobenzene; it does not react with acids. With reducing agents, it should yield hexamidobenzene, but the reduction, apparently best effected with zinc-dust and acetic acid, is attended with many difficulties.

Trianilidotrinitrobenzene, $C_6(NHPh)_3(NO_2)_3$, is obtained by allowing aniline to act on tribromotrinitrobenzene in the cold. It is an orange powder, insoluble in water, but soluble in benzene, &c., and melts at 238° . It has no basic properties.

Tetrabromodinitrobenzene, $C_6Br_4(NO_2)_2$, is formed as above mentioned in the preparation of tribromotrinitrobenzene, and in about equal quantity. Its separation is tedious, and is effected by fractional crystallisation from a mixture of alcohol and benzene. It melts at 224° , whereas Richter found the melting point to be 227 — 228° . The way in which it is formed is not understood. H. B.

Electrolysis of Phenol by Alternating Currents. By E. DRECHSEL (*J. pr. Chem.* [2], **38**, 65—74).—By distilling the liquid resulting from his former experiments (*Abstr.*, 1884, 1136), the author obtained an aqueous liquid containing red, oily drops. These were dissolved in ether, and the solution fractionated; a liquid boiling between 153° and 178° was thus obtained, which on analysis gave the formula $C_6H_{10}O$. By treating the oil with phenylhydrazine, a crystalline substance was produced; this was distilled with dilute sulphuric acid to try and obtain the above-mentioned liquid, but very little distilled over, and most of it was left in the form of black, oily drops floating on the liquid in the retort. These drops crystallised on cooling, and after recrystallisation from alcohol gave rhomboidal tables which rapidly became brown when exposed to the light. A purer product was obtained from the mother-liquor, and was further purified by sublimation in a vacuum and subsequent recrystallisation from 50 per cent. alcohol. The crystals were brilliant, white lamellæ, slightly soluble in hot water and freely soluble in alcohol; they melt at 108° , and have the formula $C_{12}H_{13}N$. This substance is isomeric with Graebe and Glaser's hydrocarbazol, which melts at 120° .

The author proposes the name *hydrophenoketone* for the substance $C_6H_{10}O$, which is isomeric with mesityl oxide, and *hydrophenanilide* for the compound $C_{12}H_{13}N$.

The author has previously noticed the formation of caproic acid by the action of the alternating current on phenol; he now explains this by supposing that hydrophenoketone is an intermediate product, produced by the alternate hydrogenation and oxidation of the phenol. This conversion of substances of the aromatic series into those of the fatty series may serve to throw light on the changes that take place among these and allied substances in the animal body.

A. G. B.

Action of Chlorine on Catechol and Orthamidophenol.

By T. ZINCKE and F. KÜSTER (*Ber.*, **21**, 2719—2730).—*Hexachlorodiketotetrahydrobenzene*, $CCl \begin{smallmatrix} \diagup CCl \cdot CCl_2 \\ \diagdown CCl_2 \cdot CO \end{smallmatrix} > CO + H_2O$, can be prepared

by dissolving catechol in 20 parts of glacial acetic acid and saturating the solution with chlorine; the mixture is kept cold at first, but as soon as tetrachlorocatechol begins to separate, the cooling is not necessary. After keeping for one or two days, the solution is poured into water, the precipitate collected, and the solution extracted with ether. It can also be prepared by passing chlorine through a well-cooled glacial acetic acid (10 parts) solution of orthamidophenol hydrochloride until the crystals of tetrachloranidophenol which separate are redissolved; on evaporating, the product separates, and is purified by washing with water. The yield by this method is as much as 80 per cent. of the theoretical quantity. It separates from a mixture of ether and light petroleum in colourless or slightly yellow crystals which contain 2 mols. H_2O , but lose 1 mol. H_2O when kept in a partial vacuum or when recrystallised from hot, light petroleum. The monohydrate is stable, but loses its water when heated at $90-95^\circ$ for a long time. It is readily soluble in alcohol, glacial acetic acid, benzene, and ether, and melts at $93-94^\circ$ with decomposition. When treated with aniline, it yields a small quantity of a compound melting at $236-237^\circ$. It liberates iodine from potassium iodide, and when reduced with stannous chloride it yields tetrachlorocatechol.

Hexachloropentenehydroxy-carboxylic acid, $\begin{smallmatrix} \diagup CCl \cdot CCl_2 \\ \diagdown CCl \cdot CCl_2 \end{smallmatrix} > C(OH) \cdot COOH$,

prepared by dissolving the preceding compound in sodium acetate or sodium carbonate and adding hydrochloric acid to the filtered solution, crystallises from dilute acetic acid with 1 mol. H_2O , and from light petroleum in small, colourless prisms. It melts at 111° , and on continued heating quickly solidifies at $140-150^\circ$, melting again at $185-186^\circ$. When the aqueous solution is heated, yellow, scaly crystals separate; this compound melts at 153° , and yields a red anilide. The *barium* salt, prepared by neutralising an alcoholic solution of the acid with barium hydrate, crystallises in needles which appear to contain alcohol (1 mol.); it is decomposed when heated at about 50° . The *methyl* salt, $OH \cdot C_6Cl_5 \cdot COOMe$, prepared by boiling hexachlorodiketotetrahydrobenzene with methyl alcohol, crystallises from light petro-

leum in colourless needles, melts at 62°, and is readily soluble in methyl and ethyl alcohol. The *ethyl* salt, obtained in like manner, crystallises from alcohol in rhombic prisms, and from hot, light petroleum in white needles. It melts at 121°, and dissolves unchanged in soda, but is insoluble in sodium carbonate. The *acetyl*-derivative melts at 85°, and is readily soluble in ordinary solvents, but insoluble in dilute soda.

Hexachloroketopentene, $\llbracket \text{CCl} \cdot \text{CCl}_2 \rrbracket \text{CO}$, is obtained when the preceding compound is dissolved in glacial acetic acid, a little hydrochloric acid added, and the solution warmed with a slight excess of a 10 per cent. chromic acid solution. It crystallises in colourless, rhombic plates, melts at 31.5°, boils at 155–158° (80 mm.), and can be distilled with steam. It is insoluble in sodium carbonate. The *anilide*, $\text{C}_5\text{Cl}_5(\text{NHPh})\text{O}$, crystallises in small, yellow needles or plates melting at 194–196°.

Pentachlorobutenecarboxylic acid, $\text{C}_5\text{Cl}_5\text{O}_2\text{H}$, prepared by dissolving the preceding compound in 10 per cent. soda, crystallises from hot, dilute acetic acid in needles or prisms, melts at 127°, and is readily soluble in ether, alcohol, and benzene, but only sparingly in light petroleum. It distils with partial decomposition, and loses hydrogen chloride when heated with concentrated sulphuric acid. When reduced with sodium amalgam, it yields a liquid acid, which has a strong, fatty-acid-like odour, and forms a readily soluble barium salt. The *ammonium* salt crystallises in white needles, melting at 178–180° with decomposition. The *barium* salt is readily soluble, but appears to be unstable in aqueous solution. The *methyl* and *ethyl* salts are liquids. The constitution of the acid is probably $\text{CCl}_2\text{C}(\text{CCl})\text{CCl}_2\text{COOH}$.

Tetrachlorocatechol, $\text{C}_6\text{Cl}_4(\text{OH})_2$, is obtained when hexachlorodiketohydrobenzene is reduced with stannous chloride in glacial acetic acid solution. It crystallises from hot dilute alcohol or benzene in slender needles, melts at 194–195°, and, when oxidised with nitric acid, yields tetrachlororthobenzoquinone, melting at 129–130° (compare Abstr., 1887, 808). The *acetyl*-derivative crystallises from acetic acid in thick needles melting at 190°.

F. S. K.

Iodine-derivative of Quinone. By K. METZELER (*Ber.*, **21**, 2554–2556).—*Diiodoquinone*, $\text{C}_6\text{H}_2\text{I}_2\text{O}_2$, is formed when diacetylquinol (1 part) is slightly warmed on a water-bath with a solution of potassium iodate (4 parts), slightly acidified with sulphuric acid. It crystallises from alcohol in yellow needles melting at 157–159°. When suspended in water and treated with sulphurous acid, *diiodoquinol* is obtained. This crystallises in slender needles of a silky lustre, melts at 142.5° (uncorr.), and dissolves readily in hot water, alcohol, ether, and glacial acetic acid. *Diacetyldiiodoquinol* crystallises in rhombic plates and in slender needles, melts at 148° (uncorr.), is insoluble in water, readily soluble in alcohol, ether, and in hot benzene and glacial acetic acid.

N. H. M.

Some New Benzene-derivatives. By M. E. G. KÖRNER and V. WENDER (*Gazzetta*, **17**, 486–494).—The authors point out how

necessary it is for the advancement of our knowledge of the chemico-physical properties and structure of the benzene-derivatives, that the various gaps in the different series should be filled, and the properties of the compounds which fill these gaps compared with those of the other analogous derivatives of the series. With this object, they have prepared several new benzene-derivatives, and at the end of the paper give in tabular form the chief chemico-physical properties of these various ortho-, meta-, and para-compounds.

Orthiodaniline, $C_6H_4I \cdot NH_2$.—When orthiodonitrobenzene (m. p. 49.5°) is acted on by the ordinary reducing agents, it is decomposed with elimination of the iodine, but this is not the case if ferrous hydroxide is employed; then the NO_2 group alone is attacked and converted into the NH_2 group. The iodonitrobenzene was obtained by the nitration of iodobenzene and also from orthonitraniline. A small quantity only of the nitro-compound should be operated on at a time (25 grams), using ferrous sulphate (250 grams) and ammonia in slight excess, diluted with its own volume of water. The mixture is heated on a water-bath for 8 to 10 hours, and when cold, the iodaniline is extracted with ether, and distilled in a current of steam. It is then dissolved in dilute sulphuric acid, agitated with ether, to remove unaltered nitro-compounds, the solution precipitated with ammonia or an alkaline carbonate, and the iodaniline redistilled in steam. The yield is more than two-thirds of the theoretical.

Orthiodaniline has a disagreeable odour, somewhat resembling that of the pyridine bases; it is less soluble in water than *pariodaniline*, the boiling solution as it cools depositing the substance in long, flexible needles of silky lustre; in other solvents it dissolves freely; exposed to air and light, it becomes brown after a time. It is much more volatile than its isomerides, and passes over easily with the vapour of water. It melts at 56.5° , and if heated sharply decomposes with evolution of iodine vapour.

When acted on with iodine, it yields Rudolph's diiodaniline, melting at 96° ; this confirms the constitution 1 : 2 : 4 for this diiodaniline. The salts of orthiodaniline are more soluble in water, but less stable than those of the corresponding isomerides, decomposing in aqueous solution unless there is a large excess of acid present. The *hydrochloride*, $C_6H_4I \cdot NH_2 \cdot HCl + H_2O$, forms short prisms; the *platinochloride* is an orange-yellow, crystalline powder. The *sulphate*, $3C_6H_4I \cdot NH_2 \cdot 2H_2SO_4$, separates from water in silky needles grouped in nodules; from alcohol in brilliant plates.

For comparison, the authors also prepared the two known iodanilines; *pariodaniline* melts at 63° ; *metaiodaniline* at 27° ; the hydrochloride of the latter crystallises in prisms.

Orthiodoacetanilide, $C_6H_4I \cdot NHAc = [1 : 2]$.—This is easily prepared by gently boiling a mixture of orthiodaniline and acetic anhydride in molecular proportion for four or five hours. Purified by crystallisation from alcohol, with use of animal charcoal, it forms slender prisms or large, hexagonal tables. It melts at 109.5 – 110° , and is much more volatile than its isomerides, subliming readily when gently heated.

Metaiodoacetanilide, $C_6H_4I \cdot NHAc = [1 : 3]$.—This, obtained like

the ortho-derivative, is more soluble than the latter, and crystallises in brilliant needles. It melts at 119.5° , and can be sublimed.

Pariodacetanilide, $C_6H_4 \cdot NHAc = [1 : 4]$.—This is less soluble than its isomerides. It crystallises from alcohol in rhombic prisms, which may be obtained of large size by spontaneous evaporation. It melts at 183° , and sublimes, but with difficulty.

Orthodiiodobenzene, $C_6H_4I_2$.—This is prepared by dissolving the iodauniline (10 grams) in hot dilute sulphuric acid (9 grams acid to 70 c.c. of water), cooling to 0° with continual agitation, adding a solution of potassium nitrite (4.5 grams) in a little water, and then excess of solution of potassium iodide in hydriodic acid of sp. gr. 1.1. After leaving the mixture for several hours at the ordinary temperature, the dark-coloured oil which separates is collected and distilled with steam in the presence of a little potash. Orthodiiodobenzene is a colourless liquid, which solidifies to a crystalline mass when cooled. It melts at 27° , and boils at 286.5° under a pressure of 751.5 mm. Its odour resembles that of its isomerides. *Nitro-orthodiiodobenzene*, $C_6H_3I_2NO_2 = [1 : 2 : 4 \text{ probably}]$. This is prepared by dissolving the diiodobenzene in nitric acid of sp. gr. 1.54, and after a few minutes diluting with water. When purified by crystallisation from alcohol, it forms small, lemon-yellow prisms which melt at 112.5° .

Orthanisidine, $NH_2 \cdot C_6H_4 \cdot OMe = [1 : 2]$ is known. The authors found the boiling point to be 218° under a pressure of 755.5 mm.

Metanisidine was prepared by the reduction of metanitransoil with tin and hydrochloric acid. It remains liquid at -12° , and boils at 243.5° under 755.5 mm. pressure. *Paranisidine* boils at 239.5° at 755 mm.

Orthacetaniside, $NHAc \cdot C_6H_4 \cdot OMe$, prepared by boiling for some hours a mixture of orthanisidine with acetic anhydride in molecular proportion, crystallises in hexagonal tables, and melts at 84° . *Metacetaniside* melts at $80-81^{\circ}$, and crystallises from water in needles or scales, and from alcohol in flat tables or elongated octahedra. *Paracetaniside* forms hexagonal tables, which melt at 127.1° .

C. E. G.

Action of Aniline on Epichlorhydrin. By A. FAUCONNIER (*Compt. rend.*, **107**, 250—252).—The base, $C_{15}H_{18}N_2O$, obtained by the action of aniline on epichlorhydrin (this vol., p. 586), crystallises from boiling alcohol in long, slender, white needles, which melt at $53-54^{\circ}$, and rapidly become violet in colour when exposed to light even in a closed vessel.

The *oxalate*, $(C_{15}H_{18}N_2O, H_2C_2O_4)_2 + 3H_2O$, separates in bundles of slender needles when an ethereal solution of the base is mixed with an aqueous solution of the acid. When purified by washing with water and recrystallisation from alcohol, it melts at $149-150^{\circ}$, and slowly becomes lemon-yellow when exposed to light.

The *platinochloride*, $C_{15}H_{18}N_2O, H_2PtCl_6 + 4H_2O$, crystallises in small, brilliant yellow lamellæ.

The *acetyl-derivative*, $C_{15}H_{17}N_2OAc + H_2O$, is obtained by heating the base for several hours with three times its weight of acetic anhydride and crystallising the product from alcohol. It forms colourless

lamellæ, which seem to be hexagonal, but which when dried become opaque and break up into prismatic crystals melting at 99—100°.

A *nitroso-derivative*, $C_{15}H_{16}N_2O(NO)_2$, is precipitated as a resin when aqueous solutions of the hydrochloride and sodium nitrite are mixed together. It crystallises from boiling alcohol in orange needles, which melt at 108—109°. Attempts to convert it into a hydrazine-derivative were unsuccessful.

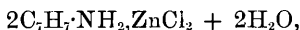
It is evident from the formation of these compounds that the base contains one hydroxyl-group, and has a double basic function. The author prefers to call it *hydroxypropylenediphenyldiamine*, and not dianilglycerol as at first proposed (*loc. cit.*). C. H. B.

Action of Aniline on Bromofumarimide. By K. LÖSCHER and R. KUSSEROFF (*Ber.*, 21, 2718—2719).—When bromofumarimide is heated with excess of aniline, a compound is obtained which has the composition of *anilidofumarimide*, and seems to have the constitution $\ll C(NHPh) - \rangle CH \cdot CO \cdot NH \gg CO$. It crystallises from hot dilute alcohol in golden-yellow plates, melts at 202°, and is readily soluble in glacial acetic acid and boiling alcohol, sparingly soluble in hot water, ether, chloroform and benzene, and insoluble in cold water. It yields an *acetyl-derivative*, and when heated with alcoholic ammonia, a crystalline compound, probably anilidofumaramide, is obtained. F. S. K.

Compounds of Organic Bases with Salts of the Heavy Metals.

By B. LACHOWICZ and F. BANDROWSKI (*Monatsh.*, 9, 510—517).—Zinc chloride forms compounds of the general formula $x(B) + yZnCl_2 + 2ZnO$, with all fatty compounds having a decidedly basic character, such as primary, secondary, and tertiary amines, neurine, and guanidine. In the aromatic series, it combines only with those primary bases which contain one benzene nucleus, or such as piperidine, pyridine, and picoline, but not with such compounds as naphthylamine.

When aniline is shaken with an aqueous solution of zinc chloride, a white, crystalline precipitate of the formula $2NH_2Ph \cdot ZnCl_2 + 2H_2O$ is formed. From hot alcohol it crystallises in long needles, which do not decompose when heated to 230°. With substituted anilines containing the negative groups Cl, NO_2 , and OH, zinc chloride does not combine, but with orthotoluidine it gives the compound

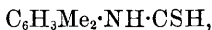


with paratoluidine, $2C_7H_7NH_2 \cdot ZnCl_2 + 3H_2O$, and with metaxylinidine, $2C_8H_9NH_2 \cdot ZnCl_2$.

α -Naphthylamine does not combine either with copper sulphate or with mercuric chloride, but with mercurous nitrate it forms a characteristic compound. β -Naphthylamine differs from its isomeride in combining with both mercuric chloride and copper sulphate.

The authors suggest that the property of combining with certain metallic salts may furnish a convenient method of isolating many organic bases. G. T. M.

Some Anhydro-bases from Unsymmetrical Metaxylidine. By E. GUDEMAN (*Ber.*, **21**, 2549—2553).—*Thioformo-xylide*,



is obtained by heating 25 grams of formo-xylide (*Abstr.*, 1885, 772) with 16 grams of phosphorus pentasulphide for 30 minutes on a water-bath, extracting the resinous product with dilute aqueous potash, and precipitating with hydrochloric acid. It crystallises from alcohol in small, slender needles melting at 105°.

Methenylamido-xylil mercaptan, $\text{C}_6\text{H}_2\text{Me}_2\langle\begin{smallmatrix}\text{N}\\\text{S}\end{smallmatrix}\rangle\text{CH}$, is formed by treating thioformo-xylide with potassium ferricyanide in alkaline solution (Jacobsen, *Abstr.*, 1886, 700). It is a heavy, yellowish liquid, of a repulsive odour.

Thioaceto-xylide, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NH}\cdot\text{CSMe}$, is prepared by heating 10 grams of aceto-xylide (m. p. 127°) for half an hour with 6 grams of phosphorus pentasulphide on a water-bath. It melts at 80°.

Ethenylamido-xylil mercaptan, $\text{C}_6\text{H}_2\text{Me}_2\langle\begin{smallmatrix}\text{N}\\\text{S}\end{smallmatrix}\rangle\text{CMe}$, obtained by adding 10 grams of thioaceto-xylide in 300 c.c. of water with 75 c.c. of 33 per cent. aqueous soda to 60 grams of potassium ferricyanide in 200 c.c. of water, is an oil.

Thiobenzo-xylide, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NH}\cdot\text{CSPH}$, is prepared by heating 50 grams of benzo-xylide with 35 grams of phosphorus pentasulphide on a sand-bath; it crystallises from alcohol in small needles, which melt at 90°.

Benzo-xylide, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NHBz}$, obtained by heating 24 grams of xylidine with 36 grams of benzoic acid for eight hours at 200—230°, and then distilling, crystallises from alcohol in long needles, which melt at 187—189°.

Benzenylamido-xylil mercaptan, $\text{C}_6\text{H}_2\text{Me}_2\langle\begin{smallmatrix}\text{N}\\\text{S}\end{smallmatrix}\rangle\text{CPh}$, obtained by oxidising thiobenzo-xylide with potassium ferricyanide, forms a white oil, which becomes greenish-yellow when exposed to air.

Ortho- and *para*-benzotoluide and *benzocumide* are readily obtained by heating the amines with an excess of benzoic acid; they are readily soluble in alcohol and in strong hydrochloric acid, insoluble in water, and melt at 131°, 154°, and 167° respectively.

N. H. M.

Dimethylaniline and Diphenylamine Sulphates. By L. VIGNON (*Compt. rend.*, **107**, 263—266).—Anhydrous dimethylaniline and sulphuric acid combine at the ordinary temperature with development of heat and formation of a crystalline acid sulphate, $\text{NMe}_2\text{Ph}\cdot\text{H}_2\text{SO}_4$, which can be purified by washing with benzene, and melts at 80°. It dissolves in water, but is insoluble in ether and in benzene. No normal sulphate is formed whatever the proportions in which the acid and base are mixed.

If the acid sulphate is heated at 180—190°, it loses water and is converted into the sulphonic acid, $\text{C}_6\text{H}_4(\text{SO}_3\text{H})\cdot\text{NMe}_2$, the barium salt of which crystallises with both 3 mols. and 5 mols. H_2O .

Diphenylamine, previously fused, likewise combines with sulphuric

acid, forming a crystalline acid sulphate whatever the proportions in which they are mixed. It has the composition $\text{NHPh}_2\cdot\text{H}_2\text{SO}_4$, and after purification by washing with benzene melts at $123-125^\circ$. The salt is insoluble in ether and benzene, and when thrown into water is decomposed, the diphenylamine separating as a flocculent precipitate.

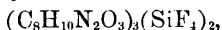
When heated at $180-190^\circ$ for two hours, the acid sulphate loses water and is converted into the sulphonic acid, $\text{C}_6\text{H}_4(\text{SO}_3\text{H})\cdot\text{NHPh}$, the barium salt of which forms anhydrous crystals.

The heats of formation of the solid salts and of aniline sulphate from the bases and dilute sulphuric acid were determined by treatment with soda with the following results:—

Aniline sulphate	16.6 Cals.
Dimethylaniline sulphate.....	8.4 „
Diphenylamine sulphate.....	4.5 „

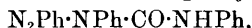
The conversion of aniline sulphate into sulphanilic acid by the action of heat is well known, and it would seem that this reaction is general. The formation of sulphonic acids is generally attributed to the dehydrating action of the excess of sulphuric acid which is always employed; but this explanation will not hold in the three cases just described. In these instances, the change is due to interatomic forces which become active at a high temperature. C. H. B.

Silicotetrafluorides of Certain Bases. By A. M. CONEY and F. W. SMITH (*Amer. Chem. J.*, **10**, 294—296; compare this vol., p. 941).—*Trinitrosodimethylaniline disilicotetrafluoride*,



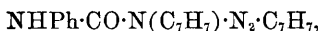
is formed by passing silicon fluoride into a solution of the base in benzene; it is bright yellow and amorphous, and decomposes completely at 150° . *Dipyridine silicotetrafluoride*, $(\text{C}_5\text{NH}_3)_2\text{SiF}_4$, is prepared in like manner; it is white, amorphous, and decomposes after a time. *Tripyridine disilicotetrafluoride*, $(\text{C}_5\text{NH}_3)_3(\text{SiF}_4)_2$, is obtained by heating the preceding substance, when pyridine is liberated, and the new compound sublimes in crystalline crusts. H. B.

Diazoamido-compounds. By H. GOLDSCHMIDT and E. MOLINARI (*Ber.*, **21**, 2557—2579).—*Diazobenzenediphenylcarbamide*,



is obtained by slightly heating a mixture of diazobenzene with phenyl cyanate in molecular proportion, dissolved in light petroleum; on cooling, it separates as an almost white, crystalline precipitate, which melts at 125° . When mixed with 10 per cent. sulphuric acid and steam-distilled, it is decomposed into phenol, phenyl cyanate, and diphenylcarbamide, the latter being partially decomposed into aniline and carbonic anhydride.

Diazobenzene:phenylparatolylcarbamide, $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{NPh}\cdot\text{NPh}$, prepared in a manner similar to the diphenylcarbamide, crystallises in slender, microscopic needles melting at 134° . It is decomposed by acids into paratolylphenylcarbamide, aniline, paratoluidine, ditolylcarbamide, and phenol.

Paradiazotolueneparatolylphenylcarbamide,

forms slender, white needles, melts at 116° , and is decomposed by acid with formation of paratolylphenylcarbamide, aniline, toluidine, diphenylcarbamide, and paracresol.

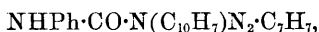
Paradiazotolueneparaditolylcarbamide, $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{N}(\text{C}_7\text{H}_7)\cdot\text{N}_2\cdot\text{C}_7\text{H}_7$, crystallises in long, white needles melting at 140° .

Diazobenzeneparatolylphenylcarbamide, $\text{NHPh}\cdot\text{CO}\cdot\text{N}(\text{C}_7\text{H}_7)\cdot\text{N}_2\text{Ph}$, is formed when an ethereal solution of diazoamidobenzenetoluene (from diazobenzene chloride and toluidine) is warmed with phenyl cyanate; it is a white precipitate consisting of slender needles, and may be purified by extraction with boiling ether; it melts at 126° . When decomposed with sulphuric acid, paratolylphenylcarbamide, as well as aniline, paratoluidine, phenol, paracresol, and phenyl cyanate, are formed. This reaction establishes the constitution of the carbamide as given, and also that of the diazoamidobenzenetoluene, which is $\text{N}_2\text{Ph}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$.

Diazobenzeneparaditolylcarbamide, $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{N}(\text{C}_7\text{H}_7)\cdot\text{N}_2\text{Ph}$, prepared from diazoamidobenzenetoluene and paratolyl cyanate, forms small, thick, lustrous prisms melting at 130° . It is decomposed by sulphuric acid into paraditolylcarbamide, aniline, paratoluidine, phenol, and paracresol.

Diazobenzene- β -naphthylphenylcarbamide, $\text{NHPh}\cdot\text{CO}\cdot\text{N}(\text{C}_{10}\text{H}_7)\cdot\text{N}_2\text{Ph}$, forms microscopic needles melting at 123° . When treated with acids, naphthylphenylcarbamide, $\text{C}_{17}\text{H}_{15}\text{N}_2\text{O}$, is formed. This compound is also prepared by the action of phenyl cyanate on β -naphthylamine; it crystallises in short, white, lustrous prisms melting at 220 – 221° .

Diazoamidotoluene- β -naphthalene, $\text{C}_{17}\text{H}_{15}\text{N}_3$, is prepared by the action of β -diazonaphthalene chloride (1 mol.) on paratoluidine (1 mol.) suspended in a solution of sodium acetate. It crystallises from benzene in slender, bright-yellow needles melting at 131 – 132° .

Paradiazotoluene- β -naphthylphenylcarbamide,

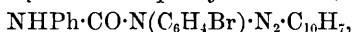
forms slender, white needles melting at 110° .

Parabromodiazoo-amidobenzenetoluene, $\text{C}_7\text{H}_7\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br}$, forms long, yellow, lustrous needles melting at 126° . *Paradiazotolueneparabromodiphenylcarbamide* forms slender needles, and melts at 124° ; when decomposed by acid, it yields parabromodiphenylcarbamide melting at 245° , and other products.

Diazobenzeneparabromodiphenylcarbamide, $\text{C}_{19}\text{H}_{15}\text{BrNO}_4$, is obtained by the action of phenyl cyanate on parabromodiazooamidobenzene; it melts at 115° , and yields parabromodiphenylcarbamide when decomposed by acids.

Diazobenzeneparabromophenylparatolylcarbamide, from phenyl cyanate and parabromodiazooamidobenzene, melts at 138° .

Parabromodiazooamidobenzene- β -naphthalene, $\text{C}_{16}\text{H}_{12}\text{BrN}_3$, is obtained by the action of β -diazonaphthalene chloride on parabromaniline in presence of sodium acetate, and crystallises from benzene in yellow prisms melting at 164° .

β-Diazonaphthaleneparabromodiphenylcarbamide,

forms white needles melting at 139—140°. When boiled with acids, parabromophenol, *β*-naphthol, and parabromodiphenylcarbamide are formed.

Paranitrodiphenylcarbamide, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, obtained by the action of phenyl cyanate on paranitrodiazoamidobenzene, crystallises from hot dilute alcohol in bright-yellow crystals, melting at 202°. It is decomposed by potash into carbonic anhydride, aniline, ammonia, and paranitrophenol.

Diazobenzeneparanitrodiphenylcarbamide,

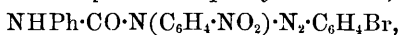
is formed when phenyl cyanate is added to an ethereal solution of paradinitrodiazoamidobenzene. It crystallises in groups of white needles melting at 115°, and dissolves in hot benzene with evolution of gas and formation of paranitrodiphenylcarbamide.

Metanitrodiazoamidobenzene, $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_2$, crystallises in yellow, pointed, thick prisms melting at 131°.

Diazobenzenemetanitrodiphenylcarbamide, $\text{C}_{19}\text{H}_{15}\text{N}_5\text{O}_3$, separates in slender, branched needles melting at 104°, when an ethereal solution of the diazo-compound is warmed with phenyl cyanate and treated with light petroleum.

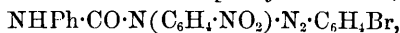
Metanitrodiazoamidobenzenetoluene, $\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}_2$, crystallises in lustrous, gold-coloured needles melting at 107°. When the ethereal solution is warmed with phenyl cyanate, *paradiazotoluenemetanitrodiphenylcarbamide*, $\text{NHPh}\cdot\text{CO}\cdot\text{N}(\text{C}_6\text{H}_4\cdot\text{NO}_2)\cdot\text{N}_2\cdot\text{C}_6\text{H}_5$, is obtained; this crystallises in white needles melting at 96°. When the solution in benzene is boiled, metanitrodiphenylcarbamide melting at 197° is formed.

Paranitroparabromodiazoamidobenzene, $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, crystallises in orange-red, lustrous needles melting at 184°.

Parabromodiazobenzeneparanitrodiphenylcarbamide,

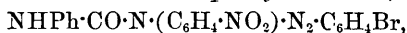
forms small crystals melting at 129°. When treated with dilute sulphuric acid, paranitrodiphenylcarbamide (m. p. 202°) is formed.

Metanitroparabromodiazoamidobenzene, $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, crystallises in groups of yellow needles melting at 155°.

Parabromodiazobenzenemetanitrodiphenylcarbamide,

forms microscopic needles melting at 134°. Sulphuric acid acts on it, yielding metanitrodiphenylcarbamide melting at 197°.

Metanitrometabromodiazoamidobenzene, $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, prepared from metanitrodiazobenzene chloride and metabromaniline, crystallises in yellow needles melting at 106°.

Metabromodiazobenzenemetanitrodiphenylcarbamide,

melts at 128°. When decomposed by sulphuric acid, metanitrodiphenylcarbamide (m. p. 196°) is formed.

N. H. M.

New Phenylhydrazine Salts. By W. H. RICHARDSON (*Chem. News*, 58, 39—40).—The author has prepared phenylhydrazinehydroxyazonaphthalenesulphonic acid by adding aqueous phenylhydrazine hydrochloride to a solution of hydroxyazonaphthalenesulphonic acid acidified with hydrochloric acid; the brown, flocculent precipitate which first forms becomes scarlet and crystalline on adding the hydrazine. The yield is quantitative; the substance is sparingly soluble in water, easily in alcohol or acetic acid, but is decomposed by boiling with dilute acids or alkalis. The corresponding barium, calcium, and magnesium salts were prepared.

Phenylhydrazine dinitro- α -naphtholsulphonate is obtained as a crystalline precipitate when aqueous phenylhydrazine hydrochloride is added to 1 gram of naphthol-yellow dissolved in a litre of water. It is sparingly soluble in boiling water, and crystallises from that medium in light brown needles. D. A. L.

Action of Nitroso-bases on Phenylhydrazine. By O. FISCHER and L. WACKER (*Ber.*, 21, 2609—2617).—The analyses of the compound obtained by the action of phenylhydrazine on nitrosoaniline point rather to the formula $C_{12}H_{12}N_4O$ than to that previously given (this vol., p. 460); paraphenylenediamine is formed in the reaction.

Nitrosodimethylaniline (3 mols.) reacts with phenylhydrazine acetate (2 mols.) with formation of the compound $C_{14}H_{16}N_4O$. This is obtained in splendid, yellow needles or plates by carefully adding water to the alcoholic solution; it melts at 103° with decomposition, and detonates when heated quickly. When the solution in chloroform is heated, it decomposes with explosive violence and liberation of carbonic anhydride.

Free phenylhydrazine reacts with nitrosodimethylaniline dissolved in ether with formation of parazodimethylaniline, dimethylphenylenediamine, and an oil. When an alcoholic solution is used, a small amount of parazodimethylaniline, together with some dimethylphenylenediamine and dimethylamidodiphenylamine, $NHPh \cdot C_6H_4 \cdot NMe_2$, are obtained. The latter crystallises from light petroleum in needles which melt at 130° and sublime below 100° ; it is readily soluble in dilute hydrochloric, less in dilute sulphuric acid. When the dilute acid solution is treated with sodium nitrite, the nitrosamine, $C_{14}H_{16}N_3O$, is formed. This crystallises in slender, pale yellow needles which melt at 116° with decomposition.

Benzenediazonitrosodiphenylamine, $C_{18}H_{16}N_4O$, obtained by the action of phenylhydrazine on nitrosodiphenylamine in acid solution, crystallises in lustrous, gold-coloured plates, which become greenish when exposed to light; it melts with decomposition at 112° and detonates when quickly heated.

Free phenylhydrazine dissolved in ether acts on nitrosodiphenylamine, yielding amidodiphenylamine melting at 75° , and azoxydiphenylamine, $C_{24}H_{20}N_4O$, which crystallises in splendid, gold-coloured plates melting at 173° . When an alcoholic solution is used instead of an ethereal solution, Calm's paradiphenylphenylenediamine (*Abstr.*, 1884, 594) is formed. This melts at 145° (not 152°).

Parazoxyphenol, $ON_2(C_6H_4 \cdot OH)_2$, is formed, together with paramido-

phenol, when equal parts of nitrosophenol and phenylhydrazine are treated with ether (5—6 parts). It crystallises from dilute alcohol in pale-yellow, lustrous plates with 1 mol. H_2O ; the hydrate has probably the constitution $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{OH})\cdot\text{N}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{OH}$.

N. H. M.

Action of Secondary Aromatic Amines and Hydrazines on Bromacetophenone. By J. CULLMANN (*Ber.*, **21**, 2595—2597).—When bromacetophenone (1 mol.) and methylaniline (2 mols.) are mixed, heat is developed, and on cooling the whole solidifies; the product contains Stadel and Siepermann's phenacylmethylanilide (*Abstr.*, 1881, 722). When this is heated with zinc chloride (5 parts) at 180° , 1' : 2'-methylphenylindole melting at 101° is formed (Degen, *Abstr.*, 1887, 145).

When bromacetophenone and methylaniline are heated to boiling, a violent reaction takes place with formation of 2'-phenylindole and another compound, probably 1' 2'-methylphenylindole.

*Phenylglyoxal*methylphenylosazone, $\text{NMePh}\cdot\text{N}:\text{CPh}\cdot\text{CH}:\text{N}\cdot\text{NMePh}$, is formed when a solution of methylphenylhydrazine (3 mols.) dissolved in alcohol (5 parts) at 0° is treated with bromacetophenone (1 mol.). After some hours, the whole becomes dark-red, and is then kept for a week at the ordinary temperature; it is filtered, washed with ether, and crystallised from hot alcohol, from which it separates in yellowish-red prisms melting at 151° .

N. H. M.

Osazones. By H. v. PECHMANN (*Ber.*, **21**, 2751—2762).—To detect the presence of an osazone, the substance is moistened with alcohol, gently warmed with a little ferric chloride, and the mixture shaken with ether; if an osazone is present, the ether is coloured red or reddish-brown. This reaction depends on the fact that the osazones of simple 1.2-diketo-derivatives are very readily converted into coloured, crystalline substances when treated with oxidising agents. Only those osazones which are derived from simple, fatty diketo-compounds or those which contain but one aromatic radicle give this reaction. Tartrazine and the osazones of benzil, acetyl-glyoxylic acid, dehydroxytartaric acid and glucose do not show the reaction. Acetyl-glyoxylic acid osazone yields pyrazolone-derivatives when treated as described above. The coloured oxidation products of osazones, which the author names *osotetrazones*, are neutral substances containing 2 atoms of hydrogen less than the osazones.

Diacetyl-osazone is best prepared as follows:—A mixture of 14.4 parts of methyl acetoacetate, 250 parts of water, and 48 parts of soda (1 : 5) is kept for about 24 hours, 7 parts of sodium nitrite added, and finally dilute sulphuric acid gradually poured into the well-cooled solution until the liquid just colours tropæolin paper violet, the whole being well agitated. After adding soda until the solution becomes yellow, it is acidified with acetic acid and mixed with 10.8 parts of phenylhydrazine in 30 parts of 50 per cent. acetic acid, the whole being well stirred. The *hydrazoxime*, melting at 158° , which separates from the solution is collected, washed, dried, and heated at 100° for about an hour with two-thirds of its weight of phenylhydrazine dissolved in 50 per cent. acetic acid. The osazone, which separates

almost completely, is collected, washed, and dried. 144 grams of methyl acetoacetate yield 180 grams of the osazone.

Diacetylosotetrazone, $\langle \text{CMe:N:NPh} \rangle$, is prepared by heating the osazone (5 parts) with potassium dichromate (4 parts), water (20 parts), and 50 per cent. acetic acid (5 parts), until the solution begins to become turbid. It crystallises from boiling alcohol in dark claret-coloured, flat needles, melts at 169° with decomposition, and is soluble in chloroform and benzene, more sparingly soluble in ether, acetone, and alcohol, almost insoluble in glacial acetic acid, and insoluble in water; the solutions are brownish-red. It dissolves in concentrated sulphuric acid with a blue coloration which immediately changes to a dirty brown; when warmed with phenylhydrazine, it yields a red solution, which at a higher temperature becomes colourless and contains the osazone, which is precipitated in a pure state on adding alcohol.

Methylglyoxalosotetrazone, $\langle \text{CH:N:NPh} \rangle$, is prepared in like manner from methylglyoxalosazone (Abstr., 1887, 1104) which is best obtained by the method described in the case of diacetylosazone. The yield is quantitative. It crystallises from boiling alcohol in needles, somewhat lighter coloured and rather more readily soluble than, but otherwise similar to, those of the diacetyl-derivative. It melts at $106\text{--}107^\circ$, decomposes at 124° , and behaves towards sulphuric acid and phenylhydrazine similarly to diacetylosotetrazone. In the preparation of methylglyoxalosazone a crystalline hydrazoxime, $\text{CMe:N}_2\text{HPh}\cdot\text{CH:NOH}$, is obtained.

Glyoxalosotetrazone, prepared from glyoxalosazone, crystallises from alcohol in dark-red plates melting at 152° with decomposition.

When osazones or osotetrazones are boiled with dilute hydrochloric acid, they are decomposed into aniline and neutral, non-volatile, very stable, oily compounds which the author names *osotriazones*.

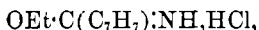
Dimethylphenylosotriazone, $\text{C}_2\text{Me}_2\text{N}_3\text{Ph}$, can be obtained by warming diacetylosotetrazone with 6 to 7 parts of water and $1\frac{1}{2}$ parts of concentrated hydrochloric acid until it is wholly converted into a brown oil, and then distilling the product with steam. An addition of $1\frac{1}{2}$ parts of 50 per cent. ferric chloride solution increases the yield. In this reaction, considerable quantities of diacetylhydrazone are formed, and when the decomposition of the osotetrazone is carried out in alcoholic solution, this hydrazone is the principal product. Dimethylphenylosotriazone can also be prepared by gradually adding phosphoric chloride (40—45 grams) to a chloroform (300 grams) solution of the hydrazoxime referred to above. The reaction product is carefully mixed with water and the chloroform solution separated, washed, filtered, and evaporated. The osotriazone obtained by either of these methods is treated with alkaline potassium permanganate until the colour of the latter is permanent, distilled with steam, extracted with ether, and fractionated under diminished pressure. It is a colourless oil, but solidifies on cooling, forming a crystalline substance which melts at 35° and boils at about 255° (at 192° , 60 mm.). It is almost insoluble in water but soluble in all other liquids. It dissolves

in concentrated acids but is reprecipitated by water. The *picrate* is crystalline. It dissolves unchanged in fuming nitric acid, but on adding concentrated sulphuric acid, it forms a *nitro*-derivative which, after recrystallisation from alcohol, is obtained in white needles melting at 227°. It is very stable towards reducing agents and is not acted on by hydriodic acid and phosphorus at 200°. When treated with sodium and alcohol, it yields small quantities of aniline and other bases. It is acted on by oxidising agents only after prolonged boiling, and when thus treated with alkaline potassium permanganate it yields a crystalline acid, probably bibasic. The constitution of this osotriazone is probably $\text{<CMe:N \over CMe:N>NPh}$.

Methylphenylosotriazone, $\text{C}_2\text{HMeN}_3\text{Ph}$, is prepared by treating methylphenylosotetrazone with hydrochloric acid as described above. It is a colourless oil, boils at 149–150° (60 mm.), and resembles the preceding compound, from which it differs however in the following reactions:—When treated with sodium and alcohol, it forms a deep-red solution which is decolorised on adding water. Salts of diazobenzene produce a brownish-red precipitate in aqueous alcoholic solutions.

Phenylosotriazonecarboxylic acid, $\text{COOH}\cdot\text{C}_2\text{HN}_3\text{Ph}$, is obtained when methylphenyltriazone is boiled with alkaline potassium permanganate for a long time, and the unaltered oil distilled with steam. It crystallises in needles, melts at 191–192°, and is soluble in alcohol, ether, and chloroform, but almost insoluble in cold water. It distils undecomposed when heated alone, but it is not volatile with steam. When treated with sodium amalgam in the cold, it is readily reduced, yielding aniline and other basic products. The *barium* salt crystallises from water and is sparingly soluble. The *silver* salt, $\text{C}_6\text{H}_5\text{AgN}_3\text{O}_2$, is stable, and when distilled, yields an oil which shows the reaction of methylphenyltriazone with alcohol and sodium, and is probably phenylosotriazone. F. S. K.

Paratolenylimido Ethyl Ether. By G. GLOCK (*Ber.*, 21, 2650—2659).—*Paratolenylimido ethyl ether hydrochloride*,

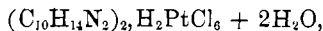


prepared by saturating an alcoholic ethereal solution of paratolunitrile with hydrogen chloride, melts at 161° with decomposition, is readily soluble in alcohol, insoluble in ether and benzene, and is decomposed by water into ethyl paratoluate and ammonium chloride. When heated at 200°, it yields ethyl chloride and toluamide. The *platinochloride*, $(\text{C}_{10}\text{H}_{13}\text{NO})_2\cdot\text{H}_2\text{PtCl}_6 + 2\text{H}_2\text{O}$, is crystalline but unstable. The free *base* is a liquid; it is decomposed into tolunitrile and ethyl alcohol when distilled, and when kept for a long time, a polymeric compound separates in long needles; this melts at 260°, and is sparingly soluble in hot alcohol and insoluble in water.

Paratolenylimidoacetate, $\text{OAc}\cdot\text{C}(\text{C}_6\text{H}_4)\text{:NH}$, prepared by heating the hydrochloride of the imidoether with acetic anhydride and sodium acetate, crystallises in prisms, melts at 147°, is readily soluble in alcohol, sparingly soluble in water, and insoluble in ether.

Tolenylamidine hydrochloride, $\text{NH}_2\cdot\text{C}(\text{C}_7\text{H}_7)\cdot\text{NH}\cdot\text{HCl}$, crystallises in prisms with $\frac{1}{2}$ mol. H_2O , melts at 213° , and is readily soluble in water and alcohol but insoluble in ether. The free *base* crystallises in nacreous plates, melts at $101\text{--}102^\circ$, and is soluble in alcohol and ether. The *platinochloride*, $(\text{C}_8\text{H}_{10}\text{N}_2)_2\cdot\text{H}_2\text{PtCl}_6$, crystallises in bright yellow needles, melts at 225° , and is sparingly soluble in water. The *nitrate*, $\text{C}_8\text{H}_{10}\text{N}_2\cdot\text{HNO}_3 + 2\text{H}_2\text{O}$, is crystalline, melts at 95° , and is readily soluble in water. The *sulphate* $(\text{C}_8\text{H}_{10}\text{N}_2)_2\cdot\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$, crystallises in prisms melting at 240° , and is readily soluble in water.

Dimethyltolenylamidine hydrochloride, $\text{NHMe}\cdot\text{C}(\text{C}_7\text{H}_7)\cdot\text{NMe}\cdot\text{HCl}$, the reaction product of tolenylimido ethyl ether hydrochloride and methylamine, crystallises in long, silky needles, melts at 200° , and is readily soluble in water and alcohol. The *platinochloride*,



forms quadratic crystals and melts at 95° . The hydrochloride of the isomeric compound, $\text{NMe}_2\cdot\text{C}(\text{C}_7\text{H}_7)\cdot\text{NH}$, is obtained when dimethylamine is employed in the place of methylamine in the above reaction. It crystallises in prisms.

Ethyltolenylamidine platinochloride, $(\text{C}_{10}\text{H}_{14}\text{N}_2)_2\cdot\text{H}_2\text{PtCl}_6 + 4\text{H}_2\text{O}$, crystallises in long needles and melts at 65° . *Diphenyltolenylamidine*, $\text{NHPh}\cdot\text{C}(\text{C}_6\text{H}_5)\cdot\text{NPh}$, crystallises in white plates, melts at 168° , and is readily soluble in alcohol, ether and benzene, but insoluble in water.

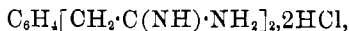
The compound, $\text{NH}\cdot\text{C}(\text{NH})\cdot\text{C}_7\text{H}_7\cdot\text{CH}_3$, is obtained, together with toluic acid, when paratolenylamidine is boiled with sodium acetate and acetic anhydride. It crystallises in needles, melts at $152\text{--}153^\circ$, and is almost insoluble in all ordinary solvents.

Tolylmethylhydroxypyrimidine, $\text{C}_7\text{H}_7\cdot\text{C}\begin{smallmatrix} \text{N}—\text{CMe} \\ \text{N}:\text{C}(\text{OH}) \end{smallmatrix}\text{CH}$, is formed when tolenylamidine is heated with ethyl acetoacetate. It crystallises in long needles, melts at 216° , is readily soluble in chloroform and moderately soluble in hot alcohol, but insoluble in water. The *platinochloride*, $(\text{C}_{12}\text{H}_{12}\text{N}_2\text{O})_2\cdot\text{H}_2\text{PtCl}_6 + 2\text{H}_2\text{O}$, crystallises in bright yellow needles and melts at 241° . The *picrate*, $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, forms yellow needles, melts at 296° , and is readily soluble in alcohol and hot water, but only sparingly in cold water. The *dichromate*, $(\text{C}_{12}\text{H}_{12}\text{N}_2\text{O})_2\cdot\text{H}_2\text{Cr}_2\text{O}_7 + 7\text{H}_2\text{O}$, crystallises in yellow plates melting at about 170° .

F. S. K.

Phenylene-paradiacetimido Ethyl Ether. By G. GLOCK (*Ber.*, **21**, 2659—2664).—*Phenylene-paradiacetimido ethyl ether hydrochloride*, $\text{C}_6\text{H}_4\cdot[\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{OEt}]_2\cdot 2\text{HCl}$, prepared by treating paraxyllylene cyanide with hydrogen chloride in alcoholic solution, crystallises in needles, melts above 240° , and is readily soluble in alcohol but insoluble in benzene and ether. It is hygroscopic and decomposes on exposure to the air or when dissolved in water.

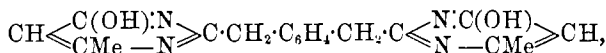
Phenylene-paradiacetamidine hydrochloride,



crystallises in prisms, is readily soluble in water and alcohol, and does not melt when heated to 240° . The free *base* crystallises in plates,

melts at 182°, is readily soluble in benzene, alcohol, and ether, and absorbs carbonic anhydride from the air.

Xylyleneparadimethylhydroxypyrimidine,



prepared by treating phenylenediacetimido ethyl ether (1 mol.) with ethyl acetoacetate (2 mols.), is crystalline, melts at 250°, and is insoluble in ordinary solvents.

Amidotolunitrile, prepared from metanitrotolunitrile, crystallises in white plates, melts at 93°, and is readily soluble in alcohol, ether, and benzene, but insoluble in light petroleum.

Homophthalonitrile, prepared from the preceding compound by Sandmeyer's method, crystallises in slender, white needles, melts at 117°, and is readily soluble in alcohol and benzene but insoluble in light petroleum.

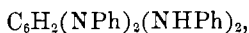
Metacyanoparatolenylimido ethyl ether hydrochloride,



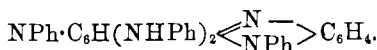
prepared by passing hydrogen chloride into an alcoholic benzene solution of homophthalonitrile, crystallises in prisms and melts at 199°.

F. S. K.

Azophenine and Induline. By O. FISCHER and E. HEPP (*Ber.*, 21, 2617—2624; compare this vol., p. 472).—When azophenine (400 grams) is boiled with alcohol (40 litres) and strong sulphuric acid (2 kilos.) for 10 hours, quinonedianilide (195 grams) and induline (20 grams) are formed (compare *Abstr.*, 1887, 1105). This reaction and v. Bandrowski's synthesis of azophenine from diphenylparazophenylene (this vol., p. 1081) confirm the formula



previously ascribed to azophenine. The constitution of induline obtained by the addition of aniline to azophenine is probably—



When nitrosodiphenylamine (10 grams) is heated with aniline hydrochloride (12 grams) and water (1 litre) for two hours in a water-bath, phenylsafranin (identical with Perkin's pseudomauveine), a soluble induline, and aniline-black are formed.

Rosinduline, $\text{NPh} \cdot \text{C}_{10}\text{H}_5 \begin{array}{c} \text{N} - \\ \text{NPh} \end{array} \gg \text{C}_6\text{H}_4$, is prepared by adding nitrosoethyl- or nitrosophenyl- α -naphthylamine (1 part) to a mixture of aniline hydrochloride (1 part) and aniline (3 to 4 parts), heated to 90°, and afterwards heating the whole for some hours at 110—120°. The product is treated first with water, then with dilute hydrochloric acid, the residue extracted with boiling alcohol, and after being diluted with water, filtered and precipitated with ammonia. It forms lustrous, garnet-coloured plates, which melt at 235°, and dissolve in benzene, but are less soluble in alcohol, and almost insoluble in water. The *platino*-

chloride, $(C_{28}H_{19}N_3)_2 \cdot H_2PtCl_6$, forms reddish-yellow crystals; the *hydrochloride* crystallises in thick, reddish-brown prisms with lustrous, gold-coloured surfaces, sparingly soluble in water, more readily in alcohol. The crystals from dilute alcohol contain $1\frac{1}{2}$ mol. H_2O . The *acid sulphate*, $C_{28}H_{19}N_3 \cdot H_2SO_4$, crystallises from dilute alcohol in bronze-coloured prisms with 1 mol. H_2O . The *nitrate* forms needles or prisms of a bronze-like lustre, and melts at 231° . The *picrate* crystallises in lustrous plates. When the base is heated with hydriodic acid and amorphous phosphorus at 150° , aniline hydriodide and a hydriodide, $C_{22}H_{13}N_2 \cdot HI$, are formed. If the reduction takes place at 200° , a large amount of aniline hydriodide is obtained together with a neutral substance which seems to be a mixture of di- and tetra-hydronaphthalene.

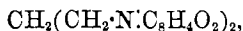
N. H. M.

Benzotribromanilide. By S. BORRELLI (*Gazzetta*, 17, 527—528).—This compound is obtained on gently heating a mixture of symmetrical tribromaniline with benzoic chloride in molecular proportion until hydrogen chloride ceases to be evolved, washing the product with a warm solution of sodium carbonate, and crystallising the residue from alcohol. *Benzotribromanilide*, $C_6H_3Br_3 \cdot NHBz$, forms stellate groups of needles melting at 198° .

If the anilide is dissolved in cold nitric acid of sp. gr. 1.5 and the solution poured into much water, a yellowish, flocculent precipitate is produced which is a mixture of nitro-derivatives. By treatment with alcohol, the product may be separated into three portions, one insoluble, another very soluble, and a third moderately soluble. The insoluble portion, which is left as colourless, silky needles, melts at 272 — 273° , and is a dinitro-derivative, $C_{13}H_6Br_3(NO_2)_2NO$. The fraction which is moderately soluble also crystallises in colourless, silky needles melting at 227° . It is likewise a dinitro-derivative isomeric with the insoluble one. Nothing definite could be separated from the very soluble fraction.

C. E. G.

Derivatives of Propylamine. By S. GABRIEL and J. WEINER (*Ber.*, 21, 2669—2679).—*Trimethylenediphtalimide*,



prepared by heating a mixture of trimethylene bromide (1 mol.) and potassium phthalimide (2 mols.) at about 170° , crystallises in slender, white needles, melts at 197 — 198° , is sparingly soluble in ether, carbon bisulphide, chloroform, and cold alcohol, moderately soluble in hot glacial acetic acid, and almost insoluble in water and light petroleum. It yields phthalic acid and trimethylenediamine hydrochloride when heated at 180 — 200° with concentrated hydrochloric acid.

Trimethylenediphtalamic acid, $C_3H_8(NH \cdot CO \cdot C_6H_4 \cdot COOH)_2$, prepared by warming the imide with potash, is a white, crystalline substance which begins to decompose at 70° , and seems to be decomposed when boiled with water. It yields phthalic acid and trimethylenediamine when heated with hydrochloric acid. The *silver salt*, $C_{19}H_{16}Ag_2N_2O_8$, crystallises in prisms.

γ -Bromopropylphthalimide, $CH_2Br \cdot CH_2 \cdot CH_2 \cdot N \cdot C_6H_4O_2$, is obtained,

together with trimethylenediphthalimide, by heating a mixture of potassium phthalimide (70 grams) and trimethylene bromide (210 grams) at about 70° . The reaction product is distilled with steam, and the residual oil, which solidifies on cooling, is crystallised from boiling alcohol and extracted with ether. Trimethylenediphthalimide (6 grams) remains, and almost pure brompropylphthalimide (63 grams) is obtained when the ethereal solution is evaporated. It crystallises from light petroleum in long needles, melts at $72-73^{\circ}$, is very sparingly soluble or quite insoluble in water, and only sparingly in light petroleum, but readily in warm alcohol and ether.

γ -Hydroxypropylamine, $\text{OH}\cdot\text{C}_3\text{H}_6\cdot\text{NH}_2$, is formed, together with hydrogen bromide and phthalic acid, when the preceding compound is heated at about 200° with sulphuric acid. The reaction product is freed from phthalic acid by filtration, the filtrate treated successively with barium carbonate and silver carbonate, and the solution of the base evaporated with hydrochloric acid. The hydrochloride is a syrup. The *platinochloride*, $(\text{C}_3\text{H}_5\text{ON})_2\cdot\text{H}_2\text{PtCl}_6$, crystallises in yellow plates and is readily soluble in water. The *aurochloride*, $\text{C}_3\text{H}_5\text{ON}\cdot\text{HAuCl}_4$, is crystalline.

γ -Bromopropylamine hydrobromide, $\text{CH}_2\text{Br}\cdot\text{C}_2\text{H}_4\cdot\text{NH}_2\cdot\text{HBr}$, is obtained, together with phthalic acid and small quantities of bromethylenediamine hydrobromide, when bromopropylphthalimide is heated at $180-200^{\circ}$ with concentrated hydrobromic acid. It crystallises from alcohol in slender needles, and from ether in small plates, melts at 162° , and is readily soluble in water and alcohol. The *picrate*, $\text{C}_3\text{H}_6\text{Br}\cdot\text{NH}_2\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7 + \frac{1}{2}\text{H}_2\text{O}$, begins to melt at 115° and is completely melted at 125° ; the anhydrous salt melts at $125-127^{\circ}$.

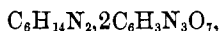
β -Bromopropylamine picrate can be prepared by saturating aqueous allylamine with hydrogen bromide, evaporating the solution, heating the residual salt with concentrated hydrobromic acid at 100° , and precipitating an aqueous solution of the product with sodium picrate. It forms compact, yellow, anhydrous crystals and melts at 154° with previous softening.

When aqueous γ -bromopropylamine hydrobromide (1 mol.) is treated with cold soda (1 mol.), a strongly alkaline solution of amine-like odour is obtained which, after acidifying, gives no precipitate with potassium bismutho-iodide solution. On heating the alkaline solution at 80° in a closed vessel, it loses its alkaline reaction almost completely, and on adding potassium bismutho-iodide to a small portion, a heavy, cinnabar-red, crystalline precipitate is formed. When this solution is saturated with alkali and distilled with steam, a distillate is obtained which contains two volatile bases but is free from allylamine. The distillate is evaporated to a syrup, the bases separated by adding potash, dried first over potash and then over sodium, and fractionated.

The base, $\text{C}_3\text{H}_7\text{N}$, probably trimethylenimine, distils between 65° and 80° . It has a strongly ammoniacal odour, fumes in the air, and is miscible with water. It combines with carbon bisulphide with explosive violence, but does not show either of Hofmann's reactions for primary amines. The *picrate*, $\text{C}_3\text{H}_7\text{N}\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, crystallises in

compact, yellow needles or granules melting at 166—167°. The *aurochloride*, $C_6H_7N, HAuCl_4$, separates in yellow, fern-like crystals, and is sparingly soluble in cold but readily soluble in hot water. The *platinochloride*, $(C_6H_7N)_2, H_2PtCl_6$, crystallises in orange-yellow needles and melts at 200—203° with decomposition.

The *base*, $C_6H_{14}N_2$, distils between 160° and 167°. It has an amine-like odour, a strongly alkaline reaction, and is miscible with water. It combines with carbon bisulphide with evolution of heat, and gives both the reactions for primary amines. The *picrate*,



separates from hot water, in which it is sparingly soluble, in indented crystals melting at about 210° with decomposition. The *aurochloride*, $C_6H_{14}N_2, 2HAuCl_4$, crystallises in yellow, microscopic plates and is rather sparingly soluble. The *platinochloride*, $C_6H_{14}N_2, H_2PtCl_6$, crystallises in orange-red plates and melts at about 215° with decomposition. The authors will continue their investigation of these bases.

F. S. K.

Action of Potassium Phthalimide on Oxyhalogen Compounds. By C. GOEDECKEMEYER (*Ber.*, 21, 2684—2692).—*Acetonylphthalimide*, $COMe \cdot CH_2 \cdot N \cdot C_6H_4O_2$, the reaction-product of potassium phthalimide and chloroacetone, crystallises from boiling water in plates and needles melting at 117°. It is rather easily soluble in alcohol, ether, benzene and acetic acid, but almost insoluble in light petroleum. The *oxime*, $NOH \cdot CMe \cdot CH_2 \cdot N \cdot C_6H_4O_2$, forms small, prismatic crystals, melting at 172°, and is readily soluble in chloroform, alcohol, and glacial acetic acid, but only sparingly in light petroleum, and almost insoluble in boiling water. The *hydrazide*, $N_2HPh \cdot CMe \cdot CH_2 \cdot N \cdot C_6H_4O_2$, separates in yellow, prismatic crystals, melts at 150—152° with decomposition; it is very sparingly soluble in hot water, but readily in most of the ordinary solvents.

Phenacylphthalimide, $COPh \cdot CH_2 \cdot N \cdot C_6H_4O_2$, prepared by heating potassium phthalimide with bromoacetophenone, crystallises from glacial acetic acid in plates, melts at 167°, and is soluble in alcohol, ether, chloroform, and benzene, but almost insoluble in water and light petroleum. The *hydrazide*, $N_2HPh \cdot CPh \cdot CH_2 \cdot N \cdot C_6H_4O_2$, crystallises from glacial acetic acid in slender, orange-yellow needles, melts at 155°, and is soluble in the ordinary solvents except water.

Phenacylphthalamic acid, $COPh \cdot CH_2 \cdot NH \cdot CO \cdot C_6H_4 \cdot COOH$, is obtained when the imide is treated with warm, alcoholic potash. It crystallises from glacial acetic acid in small needles, melts at 160°, and is soluble in almost all the ordinary solvents except water. The *silver salt*, $C_{16}H_{12}NO_4Ag$, and the copper salt are crystalline. The acid is converted into α -amidoacetophenone hydrochloride and phthalic acid when boiled with concentrated hydrochloric acid.

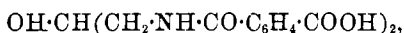
α -Amidoacetophenone picrate, $COPh \cdot CH_2 \cdot NH_2, C_6H_3N_3O_7$, crystallises in long, yellow needles, melting at 175° with decomposition.

Ethyl phthalylamidoacetate, the reaction-product of potassium phthalimide and ethyl chloroacetate, crystallises from hot alcohol or boiling water in long, white needles, melts at 112—113°, and is not

hydrolysed when boiled with water (compare Reese, this vol., p. 148). It yields amidoacetic acid, phthalic acid, and ethyl chloride when heated at 200° with concentrated hydrochloric acid.

β-Hydroxytrimethylenediphtalimide, $\text{OH}\cdot\text{CH}(\text{CH}_2\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{O}_2)_2$, is obtained in small quantities when potassium phthalimide and epichlorhydrin are heated together at 120°, and in larger quantities by heating the imide with dichlorhydrin at 145–150°. It crystallises from glacial acetic acid in white needles, melts at 204–205°, and is readily soluble in chloroform, moderately soluble in alcohol and benzene, and insoluble in water.

Hydroxytrimethylenediphtalamic acid,



is obtained in slender, white needles, when the imide is boiled with potash and the reaction-product precipitated with hydrochloric acid. It is very hygroscopic and cannot be recrystallised, as it very readily resinifies. It melts at 120°, and at 128° is reconverted into the imide. Hydroxytrimethylenediamine hydrochloride (compare Claus, *Ann.*, **168**, 36), prepared by evaporating the preceding compound with hydrochloric acid, or by heating the imide with hydrochloric acid at 165°, crystallises in small, white, hygroscopic needles, melts at 184·5° (corr.), and is very readily soluble in water, but insoluble in ether and absolute alcohol. The *picrate*, $\text{C}_3\text{H}_{10}\text{N}_2\text{O}_7\cdot 2\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, crystallises in yellow needles, and melts at 230° with decomposition. The *platinochloride*, $\text{C}_3\text{H}_{10}\text{N}_2\text{O}_7\cdot \text{H}_2\text{PtCl}_6$, crystallises in long, orange needles, and is soluble in cold water, but insoluble in alcohol and ether. It is decomposed when heated at about 240°. The *aurochloride* is crystalline and sparingly soluble. The *ferrocyanide* is similar.

F. S. K.

Amido-derivatives of Metaxylene. By R. BRÖMME (*Ber.*, **21**, 2700–2706).—*Metaxylphthalimide*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{O}_2$, is formed when metaxyl bromide and potassium phthalimide are heated together at 180–200°. It crystallises from hot alcohol in slender, white, hexagonal needles, melts at 117–118°, and is readily soluble in ether, chloroform, and alkalis.

Metaxylphthalamic acid, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, prepared by boiling the imide with soda, crystallises from hot alcohol, ether, or glacial acetic acid in slender needles melting at 131°. The *silver salt*, $\text{C}_{16}\text{H}_{14}\text{AgNO}_3$, is readily soluble in boiling water.

Metaxylamine hydrochloride, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HCl}$, is obtained, together with phthalic acid, when the imide is heated at 180–200° with concentrated hydrochloric acid. It forms compact, rhombic crystals or slender needles. The free *base* is a colourless, strongly basic-smelling liquid, boiling at 201–202° (753 mm.); it is miscible with ether and alcohol, and absorbs carbonic anhydride from the air, forming a crystalline compound. The *platinochloride*, $(\text{C}_6\text{H}_{11}\text{N})_2\cdot\text{H}_2\text{PtCl}_6$, crystallises from hot water in golden-yellow plates melting at 212°. The *sulphate*, melting at 248°, and the *oxalate*, $(\text{C}_6\text{H}_{11}\text{N})_2\cdot\text{C}_2\text{H}_2\text{O}_4$, melting at 172°, crystallise in plates, and are readily soluble in water.

The *picrate* crystallises from ether or alcohol in concentrically grouped needles melting at 156° .

Metaxylylthiocarbamide, $C_6H_4Me \cdot CH_2 \cdot NH \cdot CS \cdot HN_2$, the reaction-product of the hydrochloride of the amine and potassium thiocyanate, crystallises in white needles melting at 112° . *Dimetaxylylthiocarbamide*, $CS(C_6H_4Me \cdot CH_2 \cdot NH)_2$, prepared by boiling an alcoholic solution of the amine with carbon bisulphide, crystallises in needles, melts at 97° , and is insoluble in water, acids, and alkalis. It has a slight smell of radishes.

Metaxylylthiocarbimide, $C_6H_4Me \cdot CH_2 \cdot N \cdot CS$, is formed when a solution of the amine is evaporated with carbon bisulphide, the reaction-product mixed with mercuric chloride and distilled, or when dixylylcarbamide is heated with syrupy phosphoric acid. It yields xyllylthiocarbamide when warmed with ammonia.

Metaxylylcarbamide, $C_6H_4Me \cdot CH_2 \cdot NH \cdot CO \cdot NH_2$, crystallises from alcohol in long needles, and melts at 148° .

Dimetaxylylcarbamide, $CO(NH \cdot CH_2 \cdot C_6H_4Me)_2$, prepared by treating the amine with carbonyl chloride in ethereal solution, crystallises from alcohol or ether in slender needles melting at 137° .

Metaxylylphenylcarbamide, $NHPh \cdot CO \cdot NH \cdot CH_2 \cdot C_6H_4Me$, the reaction-product of the amine and carbamide, crystallises from alcohol, ether, or chloroform in moss-like needles, melts at 131° , and is readily soluble in benzene and glacial acetic acid.

Benzoylmetaxylylamine, $COBz \cdot NH \cdot CH_2 \cdot C_6H_4Me$, prepared by heating the amine with benzoic chloride, crystallises from alcohol in white plates, melts at 69° , and is readily soluble in chloroform, acetone, glacial acetic acid, and benzene. The *acetyl*-derivative is an oily liquid boiling at 235 – 240° .

Metaxylylenediphtalimide, $C_6H_4(CH_2 \cdot N \cdot C_8H_4O_2)_2$, prepared by heating metaxylylene bromide (26 grams) with potassium phthalimide (45 grams) at 180 – 200° , crystallises from glacial acetic acid in small needles melting at 237° .

Metaxylylenediamine hydrochloride, $C_6H_4(CH_2 \cdot NH_2)_2 \cdot 2HCl$, is obtained, together with phthalic acid, when the imide is heated at 200 – 220° with concentrated hydrochloric acid. It crystallises from hot water in long needles, and is readily soluble in dilute alcohol. The *platinochloride*, $C_6H_4(CH_2 \cdot NH_2)_2 \cdot H_2PtCl_6$, crystallises in compact, yellow plates. The free base is a colourless, basic-smelling liquid, boiling at 245 – 248° (756.5 mm.); it is miscible with alcohol and ether, but only partially miscible with water. When boiled with access of air, it absorbs carbonic anhydride, forming a white, crystalline compound. The *picrate*, $C_6H_4(CH_2 \cdot NH_2)_2 \cdot 2C_6H_3N_3O_7$, crystallises in yellow, scaly plates, and decomposes at 185 – 190° without melting. The *diacetyl*-derivative, $C_6H_4(CH_2 \cdot NHAc)_2$, is a white, crystalline compound, melting at 118 – 119° , and readily soluble in benzene, ether, alcohol, chloroform, and hot water.

F. S. K.

Benzoic Chloride as a Reagent. By L. v. UDRANSZKY and E. BAUMANN (*Ber.*, 21, 2744–2751).—When dilute aqueous solutions of fatty diamines are shaken with benzoic chloride and soda, the diamine is almost completely converted into an insoluble dibenzoyl-derivative,

which is easily separated from benzamide and other nitrogenous products by dissolving the precipitate in alcohol and pouring the solution into a large volume of water. After keeping for a short time, the dibenzoyl-derivative crystallises from the solution (compare Baumann, Abstr., 1887, 228).

A solution of 1 gram of ethylenediamine in 500 c.c. of water gave 3.5 grams of crystalline dibenzoyl-derivative when shaken with 10 grams of benzoic chloride and 80 c.c. of soda (about 10 per cent.), and further quantities can be obtained from the filtrate by repeating the operation. The mono-benzoyl-derivative is not formed in this reaction. A distinct precipitate is obtained when a solution of 5 mgrams. of ethylenediamine hydrate in 100 c.c. of water is mixed with a few drops of the reagents, and a solution containing 0.053 gram in 100 c.c. of water gave 0.133 gram of the pure dibenzoyl-derivative.

Pentamethylenediamine and tetramethylenediamine are precipitated from dilute solutions even more completely than ethylenediamine, and the dibenzoyl-derivatives can be obtained quite pure by recrystallising once or twice from alcohol or ether.

Dibenzoylpentamethylenediamine, $C_6H_{10}(NHBz)_2$, crystallises in long needles and plates which melt at 130° ; it is readily soluble in alcohol, and moderately in ether, but insoluble in water. It is not acted on by hot dilute acids or alkalis, and when dissolved in concentrated hydrochloric acid it is only changed after prolonged boiling. A solution of 0.00788 gram of pentamethylenediamine in 100 c.c. of water gave 0.0218 gram of the dibenzoyl-derivative when shaken with benzoic chloride (5 c.c.) and 40 c.c. of soda (10 per cent.), and kept for 24 hours; in a second experiment with a similar solution only 0.0142 gram of dibenzoyl-derivative was obtained.

By means of this reagent, the authors succeeded in isolating from the urine of a patient suffering from cystinuria and inflammation of the bladder, pentamethylenediamine, tetramethylenediamine, and a diamine which differed from pentamethylenediamine only in this, that its platinochloride is more readily soluble. A mixture of diamines, consisting chiefly of tetramethylenediamine, was also obtained from the fæces of the patient. Cystine was also invariably found in the urine, and it is probable that the quantity of diamines formed stands in some relation to the amount of cystine produced.

Normal urine and normal fæces do not contain even traces of diamines.

Cystine, dissolved in urine, can be isolated by means of benzoic chloride (compare Goldmann and Baumann, *Zeit. Physiol. Chem.*, 12, 254).

In the decomposition of albumin by acids, alkalis, and soluble ferments, neither cystine nor diamines are formed, but when the decomposition is caused by bacteria, diamines are soon produced, and can be shown to be present by the benzoic chloride reaction.

Compounds which contain two amido-groups combined with one and the same carbon-atom, do not yield benzoyl-derivatives when shaken with benzoic chloride and soda.

F. S. K.

Derivatives of Ethyl Benzoylacetate. By R. STIERLIN (*Ber.*, **21**, 2798).—The compounds, $C_{14}H_{12}N_2O$ (m. p. 129°) and $C_{15}H_{12}N_2O_3$ (m. p. 142°), described by the author (this vol., p. 1089), have been previously obtained by Bamberger (*Abstr.*, 1886, 62).

Cyanacetates. By A. HALLER (*Compt. rend.*, **107**, 104—107).—Ethyl cyansodacetate suspended in absolute alcohol and an acid chloride dissolved in anhydrous ether are mixed together in equal molecular proportions, and the products separated in the manner already described (*Abstr.*, 1887, 1029).

Ethyl orthotoluylycyanacetate, $C_8H_7Me \cdot CO \cdot CH(CN) \cdot COOEt$, forms modified rectangular prisms, which melt at 35.2° and remain in superfusion for a long time. It is insoluble in water, but dissolves in ethyl alcohol and ether, and the solutions give with ferric salts a red coloration. When heated with excess of water, it splits up into carbonic anhydride, ethyl alcohol, and orthomethylcyanacetophenone. The calcium-derivative of the ethereal salt crystallises with 4 mols. H_2O in small white needles, slightly soluble in water, but very soluble in ethyl alcohol.

Ethyl phenylacetylcyanacetate, $CH_2Ph \cdot CO \cdot CH(CN) \cdot COOEt$, isomeric with the preceding compound, is a yellowish oil which cannot be distilled without decomposition, and becomes viscous but does not solidify at -60° . Its solutions give a very intense red coloration with ferric salts. When heated with water, it yields carbonic anhydride, alcohol, and fusible crystals soluble in water and in ether. Its barium-derivative crystallises in white nodules, slightly soluble in water, and very soluble in alcohol. The silver-derivative is white, and insoluble in water.

Ethyl cinnamylcyanacetate crystallises in yellowish needles, which melt at 104° . It is insoluble in water, but slightly soluble in alcohol. The solution has a feebly acid reaction, but decomposes carbonates; with ferric salts it gives a red coloration. When heated with water, the ethereal salt decomposes into alcohol, carbonic anhydride, and a reddish, viscous mass which yields no crystallisable substance.

Ethyl dicinnamylcyanacetate, $CN \cdot C(CO \cdot CH : CHPh)_2 \cdot COOEt$, is obtained as a secondary product in the preparation of the preceding compound, from which it is separated by its insolubility in alkaline carbonates and in ether. It crystallises in yellowish, silky needles.

C. H. B.

Decomposition of Quinic Acid by Dilute Hydrochloric Acid. By K. CHODOUNSKI (*Chem. Centr.*, 1888, 1029, from *Listy Chem.*, **12**, 267—269).—Quinic acid was heated in sealed tubes with 3 per cent. hydrochloric acid at 100 — 120° . On opening the tubes, carbonic anhydride was evolved under considerable pressure, and in the solution phenol, quinol, and parahydroxybenzoic acid could be detected, but not trimethylbenzene.

J. W. L.

Phenaceturic Acid and its Derivatives. By E. HOTTER (*J. pr. Chem.* [2], **38**, 97—117).—To synthesise phenaceturic acid by the action of phenylacetic anhydride on glycocine, the former is dissolved in benzene and digested with very finely powdered glycocine for

10 hours in a reflux apparatus. After evaporating the benzene, the mass is extracted with ether, dissolved in hot water, decolorised, and allowed to evaporate; it is recrystallised from alcohol. The method previously published by the author (Abstr., 1887, 368) gives a better yield if the reaction is allowed to take place at -15° .

Synthetical phenaceturic acid, which is identical with the natural product, crystallises from hot water in white laminæ, and from alcohol and acetic ether in cubical crystals, melting at 143° , and decomposing completely at $190-200^{\circ}$. It is very insoluble in pure ether, sparingly so in cold water, in hot benzene, and in chloroform; very soluble in hot water, alcohol, and ethyl acetate.

If the aqueous mother-liquor from the phenaceturic acid crystals is evaporated, a mixture of this acid with a new acid is left, which can be separated by recrystallisation from alcohol. The new acid, $\text{COOH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$, analogous to Curtius' hippuramidacetic acid (Abstr., 1883, 339), melts at $173-174^{\circ}$, and crystallises in very thin laminæ, insoluble in ether, freely soluble in hot water, alcohol, and aqueous alkali.

The calcium, silver, copper, lead, and zinc salts, are described.

Methyl phenaceturate, $\text{C}_{10}\text{H}_{10}\text{NO}_3\text{Me}$, is obtained by the action of methyl iodide on the silver salt; it crystallises in long, silky needles, melting at 86.5° , easily soluble in hot alcohol, chloroform, warm ether, and benzene; it is insoluble in carbon bisulphide. The ethyl salt has been previously described (Abstr., 1887, 369).

Normal propyl phenaceturate crystallises in large rectangular plates, melting at 31° .

Phenaceturamide, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CONH}_2$, is obtained when methyl phenaceturate (1 part) is allowed to remain in contact with a 36 per cent. solution of ammonia (4 to 5 parts). It crystallises in six-sided pearly tables, melting at 174° , insoluble in cold ether and benzene, easily soluble in hot water and alcohol. By digesting an aqueous solution with yellow mercuric oxide, the mercury compound is formed, and falls as a crystalline precipitate on cooling.

Nitrophenaceturic Acid, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{COOH}$.—Phenaceturic acid (1 part) is allowed to remain in a mixture of nitric acid of sp. gr. 1.33 (4 parts) and concentrated sulphuric acid (6 parts), cooled to 0° ; the excess of the acids is filtered off, the nitro-compound dissolved in ammonia, and the solution evaporated. After decomposing the residue of ammonium salt with acid, the nitrophenaceturic acid thus obtained is recrystallised from hot water. It forms very slender needles, melting at 173° , insoluble in boiling benzene and ether, sparingly soluble in cold water and alcohol. The silver and zinc salts are described. The acid gives paranitrophenylacetic acid by prolonged digestion with strong hydrochloric acid.

Amidophenaceturic acid is obtained by dissolving the nitro-acid in yellow ammonium sulphide, passing hydrogen sulphide through the solution, heating on a water-bath until all the ammonium sulphide is decomposed, filtering, and precipitating the filtrate with dilute hydrochloric acid. The amido-acid, recrystallised from alcohol, forms rhomboidal laminæ, soluble in hot water and alcohol.

The author failed to obtain phenacetylglucolic acid by the action of

chlorine on an alkaline solution of phenaceturic acid, and of nitrous acid on an acid solution of phenaceturic acid. Nor could it be synthesised from calcium glycollate and phenylacetic chloride.

The author took phenaceturic acid for some days, but hippuric acid only was found in the urine. A. G. B.

Bromophthalic Acid. By I. GUARESCHI (*Gazzetta*, **18**, 10—13).

—This acid, the α -monobromophthalic acid, $C_6H_3Br(COOH)_2$, is obtained from dibromonaphthalene [$Br:Br = 1:4'$] by oxidation; for this purpose, the dibromonaphthalene (2 grams) is dissolved in glacial acetic acid (30 c.c.) a solution of chromic anhydride (4 grams) in acetic acid (20 c.c.) is added, and the mixture heated in a water-bath for a quarter of an hour. It is then diluted with 10 times its volume of water, filtered from the slight yellow precipitate which is formed, and evaporated at 100° . The residue is again evaporated with water, heated with sodium carbonate solution, filtered, and the filtrate acidified with sulphuric acid and repeatedly extracted with ether. On evaporating the ether, the acid is left as a white crystalline residue, which is purified by repeated crystallisation from water. It forms colourless, rhombic prisms, which melt at 178.5° with evolution of water-vapour, and leave the anhydride, which melts at 133 — 134° . This acid is soluble in water. The barium salt, $C_6H_3Br(COO)_2Ba$, obtained from the ammonium salt by double decomposition, crystallises in iridescent laminæ, which are only sparingly soluble in water. The lead salt and silver salts are white precipitates.

Monobromophthalic anhydride, $C_6H_3Br \begin{smallmatrix} CO \\ \diagup \diagdown \\ CO \end{smallmatrix} O$, sublimes in lustrous needles, and is identical with that previously obtained by the author from bromonitronaphthalene (m. p. 122.5°), by treatment with potassium permanganate, and by Meldola from dibromonaphthylamine (*Trans.*, 1885, 513). Treated with sulphuric acid and phenol, the anhydride furnishes a brominated phthalein, which gives a fine violet-purple coloration with potash.

As Nourrison (*Ber.*, **20**, 1016) has described the β -acid, the melting point of which is 168° , Faust and v. Pechmann's acid, melting at 138 — 140° , is probably a mixture of the α - and β -acids. C. E. G.

α -Benzylhomo-orthophthalic Acid. By G. EICHELBAUM (*Ber.*, **21**, 2679—2683).— α -Benzylhomo-orthophthalonitrile,



is prepared by treating an alcoholic solution of cyanobenzyl cyanide (1 mol.) and benzyl chloride (1 mol.) with potash (1 mol.). It crystallises from alcohol in colourless plates, melts at 109 — 110° , and distils above 300° . It is readily soluble in benzene, chloroform, acetone, and hot alcohol, but almost insoluble in cold alcohol, and insoluble in water, alkalis, and acids.

Benzylhomo-orthophthalamide, $CONH_2 \cdot C_6H_4 \cdot CH(C_7H_7) \cdot CONH_2$, prepared by dissolving the nitrile in concentrated sulphuric acid, crystallises from boiling alcohol in small plates, melts at 224° with evolution

of ammonia, and is soluble in alcohol, benzene, and chloroform, but insoluble in water and alkalis.

Benzylhomo-orthophthalimide, $C_6H_4 < \begin{smallmatrix} CH(C_6H_5) \\ CO \cdot NH \cdot CO \end{smallmatrix} >$, separates in needles when the amide is heated at 100° with concentrated hydrochloric acid. It melts at 176° , boils above 300° , and is readily soluble in acetic acid, alcohol, and benzene, but insoluble in ether, chloroform, acetone, and light petroleum. It is insoluble in acids, but dissolves in alkalis with a yellow coloration, and on adding more alkali, a yellow, crystalline substance is precipitated.

Benzylhomo-orthophthalic acid, $COOH \cdot C_6H_4 \cdot CH(C_6H_5) \cdot COOH$, prepared by heating the corresponding nitrile with strong hydrochloric acid at 200 – 220° , crystallises in small prisms, melts at 154° , boils above 300° , and is soluble in alcohol and benzene, but insoluble in ether and chloroform. It dissolves in potash with a yellowish coloration.

Benzylchloroxyisoquinoline is obtained, together with an isomeric compound, when benzylhomo-orthophthalimide is heated at 200° with phosphorus oxychloride, and the product extracted with potash. The compound, which is insoluble in potash, crystallises from glacial acetic acid in colourless needles, melts at 234° , and sublimes undecomposed; its constitution is probably $C_6H_4 < \begin{smallmatrix} CH(C_6H_5) \\ CCl : N \end{smallmatrix} > CO$. The compound, soluble in potash, melts at 195° , and has probably the constitution $C_6H_4 < \begin{smallmatrix} C(C_6H_5) \\ CO \cdot NH \end{smallmatrix} > CCl$.

F. S. K.

Action of Strong Sulphuric Acid on Diphenylsuccinic Acid; Diphenesuccindone. By W. ROSER (*Annalen*, **247**, 152–159).—Reimer (Abstr., 1882, 200) obtained a compound he named dibenzyl-dicarbonide by the action of strong sulphuric acid on β -diphenylsuccinic acid. The author proposes to call this substance *diphenesuccindone*. It melts at 202° , and is partly converted into isodiphenesuccindone by treatment with sodium hydroxide. The *dioxime* crystallises in needles, and melts with decomposition about 254° .

The *diphenylhydrazide* is sparingly soluble in alcohol and acetic acid; it melts with decomposition between 260° and 270° . Diphenesuccindone, $C_{18}H_{14}$, is obtained by the reduction of diphenesuccindone with phosphorus and hydriodic acid. The hydrocarbon is freely soluble in alcohol and ether, and volatilises in a current of steam. It melts at 100° .

W. C. W.

Paranitrometamidobenzenesulphonic Acid. By E. EGER (*Ber.*, **21**, 2579–2582).—*Paranitrometamidobenzenesulphonic acid*, $NO_2 \cdot C_6H_3(NH_2) \cdot SO_3H$, is obtained by heating pure barium metamidobenzenesulphonate, dried at 120 – 130° , with acetic anhydride (2 parts) for two hours on a water-bath, dissolving in water, and evaporating almost to dryness; alcohol is added to get rid of all the free acetic acid. Barium acetylamidobenzenesulphonate crystallises from the concentrated solution in silky needles, which are washed with alcohol, and dried first at 150° and afterwards at 190° . The barium salt is

dissolved in strong sulphuric acid (5 parts), treated with the calculated amount of nitric acid previously mixed with sulphuric acid (4 parts); the product is poured into ice. The sulphonic acid crystallises in pale yellow needles, rather easily soluble in hot water, sparingly in alcohol, and almost insoluble in ether. The *potassium salt* crystallises readily from water in lustrous, gold-coloured plates; the *sodium salt* forms pale yellow, lustrous needles. When the acid is reduced with zinc-dust and a little hydrochloric acid, a phenylenediamidosulphonic acid is formed, which does not yield an azine-compound with phenanthraquinone, and which gives no yellow coloration with potassium nitrite. Both amido-groups are in the para-position; this is confirmed by the reaction of the diamido-acid with metatoluylenediamine and ferric chloride, which gives rise to a splendid violet coloration.

N. H. M.

Amidosulphonic Acids. By G. PELLIZZARI and V. MATTEUCCI (*Chem. Centr.*, 1888, 1000—1002, from *L'Orosi*, **II**, 145—157).—*Sodium phthalimidophenylsulphonate*, $C_6H_4 \cdot C_2O_2 \cdot N \cdot C_6H_4 \cdot SO_3Na$, is obtained by heating equivalent quantities of sodium sulphanilate (amidophenylsulphonate), and anhydrous phthalic acid at 250° . The mass is treated with boiling water, from which the new salt crystallises on cooling in very slender, white needles. It is readily soluble in hot water, much less so in cold. By treatment with warm aqueous alcoholic ammonia, it is decomposed into phthalimide and sodium sulphanilate. The *ammonium* and *barium* salts are prepared in a manner similar to the sodium salt, and are like it in their properties.

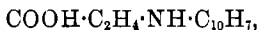
Sodium succinimidophenylsulphonate, $C_2H_4 \cdot C_2O_2 \cdot N \cdot C_6H_4 \cdot SO_3Na$, is prepared from anhydrous succinic acid and sodium sulphanilate by heating the mixture at 170° , and is purified by recrystallisation from hot water. It forms small, white crystals which are readily soluble in water, and somewhat less so in hot alcohol. The *barium* salt is similar in appearance, but is less soluble.

Carbamide and thiocarbamide react with sodium sulphanilate when heated with it, with formation of sodium carboamidophenylsulphonate and thiocarbamidophenylsulphonate respectively. These may be more readily prepared by heating potassium cyanate and thiocyanate with sulphanilic acid. They are white salts soluble in water.

Potassium phthalimidonaphthylsulphonate, $C_6H_4 \cdot C_2O_2 \cdot N \cdot C_{10}H_6 \cdot SO_3K + 3H_2O$, is prepared from potassium α -naphthylaminesulphonate and anhydrous phthalic acid by heating them together to 150° . It consists of small, shining needles.

Potassium succinimidonaphthylsulphonate, $C_2H_4 \cdot C_2O_2 \cdot N \cdot C_{10}H_6 \cdot SO_3K$, is prepared in like manner. Both this salt, as also the barium and lead salts, are white and soluble in water.

α -Naphthylsuccinimide, $C_2H_4 \cdot C_2O_2 \cdot N \cdot C_{10}H_7$, is prepared by heating potassium α -naphthylaminesulphonate with succinic acid at 200° , and extracting the fused mass with water. It forms white, shining crystals which may be distilled without decomposition. By dissolving this in hot aqueous potash, α -naphthylsuccinamic acid,



is formed, and may be precipitated from the alkaline solution by the addition of an acid. Crystallised from alcohol, it forms flattened needles melting at 171° , and is soluble in alcohol, benzene, and acetic acid. The salts of barium, silver, and copper are but little soluble.

β -Naphthylsuccinimide and the corresponding acid are prepared exactly in a similar manner to the last-named compounds, and show similar properties and solubility.

Potassium phthalimidoisethionate, $C_6H_4 \cdot C_2O_2 \cdot N \cdot C_2H_4 \cdot SO_3K + \frac{1}{2}H_2O$, is prepared by evaporating equivalent quantities of taurine and potash to dryness, adding anhydrous phthalic acid, and heating at 160° . By extracting the mass with hot water, the new compound is obtained in beautiful, colourless, monoclinic crystals. By melting the potassium salt of taurine with succinic acid, potassium succinimidoisethionate is obtained.

J. W. L.

Indene-derivatives. By W. ROSER (*Annalen*, **247**, 129—138).—Indene-derivatives are obtained by the action of sulphuric acid on diphenylsuccinic, bromocinnamic, and dichloro- and dibromo-succinic acids (Abstr., 1887, 729), also from ethyl benzylacetoacetate (Abstr., 1887, 836).

W. C. W.

Methylindenecarboxylic Acid. By W. ROSER (*Annalen*, **247**, 157—166).—The preparation and properties of γ -methylindene- β -carboxylic acid, $C_6H_4 \cdot \begin{smallmatrix} CMe \\ < \\ CH_2 \end{smallmatrix} > C \cdot COOH$, have already been described by the author (Abstr., 1887, 836). The compound $C_{11}H_{10}O_2 \cdot C_2H_4O_2$ is deposited in prisms from a solution of methylindenecarboxylic acid in glacial acetic acid. On exposure to the air, the crystals effloresce, losing acetic acid. The methyl salt melts at 78° , and dissolves easily in alcohol and ether. γ -Methylindene, $C_{10}H_{10}$, is obtained by heating the acid with soda-lime. It is a highly refractive liquid, and boils at 205 — 206° . The saturated hydrocarbon methylhydrindene has not been isolated. γ -Methylindenecarboxylic acid dibromide melts at 215° with decomposition. The methyl salt, $C_{10}H_9Br_2 \cdot COOMe$, crystallises in white needles, and melts at 157° . The preparation of α -bromo- α -methylindenecarboxylic acid has been previously described (*loc. cit.*). The methyl salt, $C_{11}H_9Br \cdot COOMe$, melts at 98 — 100° , and is soluble in alcohol and ether. It is formed when bromine is added to a solution of methyl methylindenecarboxylate in chloroform. On removing the solvent by evaporation, hydrogen bromide escapes, and methyl bromomethylindenecarboxylate remains. When a solution of bromomethylindenecarboxylic acid is saturated with hydrogen chloride, the methylic salt of chloromethylindenecarboxylic acid is produced; this is soluble in alcohol and ether, and melts at 84° ; sodium hydroxide produces an intense blue coloration in the alcoholic solution. The reduction of methylindenecarboxylic to methylhydrindenecarboxylic acid, $C_6H_4 \cdot \begin{smallmatrix} CHMe \\ < \\ CH_2 \end{smallmatrix} > CH \cdot COOH$, has been already described (*loc. cit.*). The new acid melts at 80° , and boils at 300 — 310° . The silver salt, $C_{11}H_{11}O_2Ag$, and the barium salt, $(C_{11}H_{11}O_2)_2Ba + 2H_2O$, are crystalline.

W. C. W.

Dibromindone-derivatives. By W. ROSER and E. HASELHOFF (*Annalen*, **247**, 138—151).—The authors have previously described (*Abstr.*, 1887, 830) the formation of two isomeric dibromocinnamic acids by the action of bromine on phenylpropionic acid. The α -acid melts at 139°. It is partially converted into its isomeride, melting at 100°, by recrystallisation from chloroform in presence of free bromine. The β -acid is converted into dibromindone by the action of strong sulphuric acid.

Dibromindone, $C_6H_4<\overset{CO}{\underset{CBr}{\parallel}}>Br$, forms orange-coloured needles, and melts at 123°. It dissolves in ether, chloroform, alcohol, and acetic acid, melts under water, and is volatile in a current of steam. When a mixture of α - and β -dibromocinnamic acids is treated with sulphuric acid, the α -acid remains unaltered. *Dibromindonoxime*, $C_6H_4<\overset{C(NO_2)}{\underset{CBr:CBr}{\parallel}}>$, is prepared by boiling an alcoholic solution of dibromindone with hydroxylamine hydrochloride and precipitating the product by the addition of water. It crystallises in silky needles, melts about 198° with decomposition, and forms a crystalline sodium compound. Dibromindone unites with bromine, forming *tetrabromhydrindone*, $C_6H_4<\overset{CO}{\underset{CBr_2}{\parallel}}>CBr_2$. This compound crystallises in prisms, and melts with decomposition at 124°. The alcoholic solution decomposes on boiling, yielding dibromindone. Hydroxylamine hydrochloride acts on the alcoholic solution, forming *tetrabromhydrindonoxime*, $C_6H_4Br_4NO$, melting at 214°.

Dibromindonoxime unites with bromine to form a tribromo-derivative, crystallising in golden needles and melting at 217—218° with decomposition.

Tribromovinylbenzoic acid, $CBr_2:CBr \cdot C_6H_4 \cdot COOH$, is formed when an alcoholic solution of tetrabromhydrindone is poured into excess of soda solution. The acid is soluble in alcohol and ether and crystallises in plates. It melts at 196—198°. Dibromodichlorhydrindone, or phenylenedibromodichlorethylene ketone, has been described by Zincke and Frölich (*Abstr.*, 1887, 955). It is reduced to dichlorindone by boiling with alcohol, or by treatment with sulphurous acid.

Bromiodindone is deposited in prisms on boiling an alcoholic solution of dibromindone and potassium iodide. It melts at 163°. Chlorobromindone prepared from dichlorindone melts at 105°. One atom of bromine in dibromindone is easily displaced by the action of amines, yielding anilidobromindone, piperidobromindone, &c.

Bromhydroxyindone is prepared by adding an excess of sodium hydroxide to dibromindone in presence of alcohol. The compound melts at 119°, and is freely soluble in alcohol, benzene, and acetic acid.

Dibromodiketohydrindene and chlorobromodiketohydrindene are formed by acting on an acetic acid solution of bromhydroxyindone with chlorine or bromine. The properties of these derivatives have been described by Zincke and Gerland (*this vol.*, p. 291), and by W. Wislicenus (*this vol.*, p. 1194) respectively. W. C. W.

Application of the Aluminium Chloride Method to the Naphthalene Series. By L. Roux (*Ann. Chim. Phys.*, **12**, 289—358).—The author attempted to prepare methyl-derivatives of naphthalene by Friedel and Craft's method, but without success. In one experiment in which methyl iodide was employed, a very small quantity of a hydrocarbon boiling at about 232° was isolated; it formed a crystalline picrate melting at about 120° .

When aluminium chloride (30—35 grams) is gradually added to a warm mixture of naphthalene (300 grams) and ethylene bromide (150 grams), the whole heated for about two hours, and the product fractionated, the following compounds are obtained:—(1.) A small quantity of a liquid boiling between 300° and 400° , probably consisting of a mixture of hydrides of dinaphthyl. (2.) $\beta\beta$ -Dinaphthyl. (3.) A small quantity of a hydrocarbon boiling above 450° , which is probably *dinaphthyl-naphthalene*. It crystallises from alcohol in greenish, hexagonal lamellæ, melts at about 300° , is soluble in light petroleum and toluene, and sublimes in small, yellowish scales. (4.) A mixture of α - and β -methylnaphthylene (compare Fittig and Remsen, *Ann.*, **155**, 112; and Schulze, *Abstr.*, 1884, 1183 and 1184).

Ethylnaphthalene is obtained in larger quantities when ethyl bromide is employed instead of the chloride in the method described by Marchetti (*Abstr.*, 1881, 1041; and *Gazzetta*, **11**, 439). When the product of the reaction is fractionated, almost pure ethylnaphthalene can be isolated (compare Fittig and Remsen, *loc. cit.*, and Brunel, *Abstr.*, 1884, 1035).

β -Propylnaphthalene, $C_{10}H_7Pr$, is obtained in an almost pure state when a hot mixture of naphthalene and normal propyl bromide is treated with aluminium chloride and the product fractionated. It is a colourless, highly refractive, aromatic-smelling liquid, boils at 265° , and is readily soluble in benzene, carbon bisulphide, &c., moderately so in alcohol, but insoluble in water. It yields β -naphthoic acid when boiled with dilute nitric acid. The *picrate* crystallises from alcohol or benzene in lemon-yellow needles, and melts at 89 — 90° .

β -Amylnaphthalene, $C_{10}H_7 \cdot C_5H_{11}$, is obtained almost pure when amyl chloride (from isobutyl carbinol) is treated in like manner (compare Paternò, *Bull. Soc. Chim.*, **11**, 322, and Leone, *Abstr.*, 1882, 1210). It is a colourless, aromatic-smelling liquid boiling at 288 — 292° . It yields β -naphthoic acid when oxidised with dilute nitric acid. The *picrate* crystallises from alcohol in lemon-yellow, slender needles melting at 110° .

When amyl chloride or iodide is dropped into a mixture of naphthalene and aluminium chloride at 120° , ethyldimethylmethane and dinaphthyl are formed, but amylnaphthalene is not produced.

When aluminium chloride (5—6 grams) is added to a mixture of benzyl chloride (80 grams) and naphthalene (160 grams) at 100 — 120° , and the product fractionated, dinaphthyl and a mixture of α - and β -benzylnaphthalenes are obtained. The benzylnaphthalenes can be separated by fractional crystallisation from alcohol (compare Frote, *this Journal*, 1873, 891; and Miquel, *ibid.*, 1876, ii, 407). When the

mixture of naphthalene and benzyl chloride is heated at 89—90°, only 4 to 5 grams aluminium chloride added, and the reaction stopped in 8 to 10 minutes by pouring the product into water, the α -derivative is obtained mixed with only a small quantity of the β -compound; if the mixture is heated at 160° for an hour, and the aluminium chloride added gradually during this time, the β -derivative is obtained almost free from the α -compound.

α -Benzyl-naphthalene crystallises from alcohol in colourless laminæ or prisms, melts at 59°, boils at 350°, and is very readily soluble in benzene, chloroform, and boiling alcohol, but sparingly in cold alcohol. The picrate crystallises from alcohol in golden-yellow needles and melts at 100—101°.

β -Benzyl-naphthalene, $C_{10}H_7 \cdot C_6H_5$, separates from alcohol in clinorhombic crystals, melts at 35·5°, and boils at 350°. It is very readily soluble in benzene and boiling alcohol, sparingly in cold alcohol. The picrate crystallises in golden-yellow needles melting at 93°. When α - or β -benzyl-naphthalene is oxidised with dilute nitric acid, it is converted into the corresponding naphthyl phenyl ketone.

A mixture of α - and β -methyl naphthyl ketone, $C_{10}H_7 \cdot COMe$, is obtained when the reaction-product of naphthalene, acetic anhydride, and aluminium chloride is fractionated. It is a yellowish liquid boiling at about 295°, and yields naphthoic acid and sodium acetate when heated with soda-lime. A mixture of α - and β -phenyl naphthyl ketone can be obtained by treating a mixture of naphthalene and benzoic chloride with zinc or aluminium chloride (compare Merz and Kollarits, this Journal, 1873, 1035).

F. S. K.

Oxidation of β -Naphthol to Orthocarboxycinnamic Acid. By E. EHRLICH and R. BENEDIKT (*Monatsh.*, 9, 527—532).—When to a solution of 30 grams of β -naphthol and 30 grams of potash in 1 litre of water, 50 grams of permanganate dissolved in 1 litre of water is very slowly added, orthocarboxycinnamic acid, melting at 183—184°, is formed. Its properties have been correctly described by Gabriel and Michael (*Abstr.*, 1878, 426), with the exception that these investigators give too low a melting point. Attempts to obtain the acetyl-derivative by heating it with acetic anhydride and sodium acetate were without success, the bibasic orthocarboxycinnamic acid being converted by this operation into phthalylacetic acid.

In oxidising β -naphthol by the above-mentioned method, a dye is formed as a bye-product. It can be separated from the accompanying β -naphthol by boiling with benzene, in which it is almost insoluble. It forms a greenish-blue solution with aqueous potash, dissolves readily in alcohol and glacial acetic acid, and is best recrystallised from the latter solvent.

G. T. M.

Orthamidated Aromatic Mercaptans. By P. JACOBSON (*Ber.*, 21, 2624—2631; compare *Abstr.*, 1887, 961).—In order to determine the constitution of α -amidonaphthyl mercaptan (*loc. cit.*), the ethenyl-compound, $C_{10}H_7 \cdot \begin{smallmatrix} N \\ < \\ S \end{smallmatrix} CMe$, was oxidised with permanganate in acid solution, when phthalic acid was obtained; the mercaptan has therefore the constitution $[NH_2 : SH = 3 : 4]$.

Thiocarbamidonaphthyl mercaptan, $C_{10}H_6<\overset{N}{S}>C\cdot SH$, is obtained by heating an alcoholic solution of diamidodinaphthyl sulphide,



(*loc. cit.*), with carbon bisulphide, at 110—130° for three to four hours. It crystallises from dilute alcohol in small, colourless needles which melt at above 220°. When the alkaline solution is treated with potassium ferricyanide, the *bisulphide*, $C_{10}H_6<\overset{N}{S}>C\cdot S\cdot S\cdot C<\overset{N}{S}>C_{10}H_6$, separates in needles.

β -*Thioacetonephthalide*, $C_{12}H_{11}NS$, is prepared by fusing β -acetonaphthalide (5 parts) with phosphorus pentasulphide (3 parts), extracting the product with aqueous soda, precipitating with carbonic anhydride, and crystallising from alcohol. It crystallises in needles and in tabular crystals, and melts at 145—146°. When oxidised with potassium ferricyanide, *ethenylamido mercaptan*, $C_{10}H_6<\overset{N}{S}>CMe$, is formed. This crystallises in lustrous plates, melts at 81°, and distils unchanged; the *plutinochloride* forms yellow, microscopic needles.

When ethenylamidophenyl mercaptan is heated with an equal weight of phthalic anhydride and some zinc chloride at 180° to 200° for four hours, the *phthalone*, $C_6H_4<\overset{N}{S}>C\cdot CH:C_2O_2\cdot C_6H_4$, is obtained. This forms lustrous, yellow needles, melts at above 320°, and sublimes almost without change in yellow flakes. It is sparingly soluble in hot glacial acetic acid and alcohol. The *sodium sulphonate* crystallises in orange-coloured needles.

The *phthalone* of ethenyl- α -amidonaphthyl mercaptan, $C_{20}H_{11}NSO_2$, prepared by digesting the mercaptan with phthalic anhydride (0.8 part) and some zinc chloride for two hours at 190—210°, crystallises from nitrobenzene in small, yellowish-brown, pointed needles which are still more sparingly soluble than the phenyl-derivative. When heated with strong hydrochloric acid at 220—230°, ethenylamidomercaptan and phthalic acid are formed.

N. H. M.

Isomeric Naphthyl Phenyl Ketones. By O. KEGEL (*Annalen*, **247**, 178—189).—Each of the naphthyl phenyl ketones prepared by the action of zinc on a mixture of benzoic chloride and naphthalene, yields a crystalline ketoxime when treated with an alcoholic solution of hydroxylamine hydrochloride at 100°.

The α -ketoxime melts at 140—142°. The β -ketoxime melts at 174—176°, and is less soluble in alcohol than its isomeride. Both compounds slowly undergo spontaneous decomposition, forming oily products. The ketones are converted into quinones when they are oxidised in acetic acid solution by chromic acid.

α -*Benzoylnaphthaquinone*, $C_6H_3Bz<\overset{CO\cdot CH}{CO\cdot CH}>$, crystallises in yellow needles, and melts at 152°. It is freely soluble in hot alcohol, benzene, and glacial acetic acid, and resembles α -naphthaquinone in its

properties. The *quinol* is best prepared by reducing the alcoholic solution of the quinone with stannous chloride. It is soluble in hot benzene and melts at 190—191° with decomposition. The acetic derivative formed by the action of acetic chloride on the *quinol* crystallises in plates and melts at 154—155°.

Anilido- α -benzoylnaphthaquinone is deposited in dark-red needles when an alcoholic solution of the quinone and aniline is heated at 100° for 20 minutes, and then allowed to cool. The substance melts at 199—200°. *Paratoluido- α -benzoylnaphthaquinone* melts at 196—197°. This and the preceding compound dissolve in dilute sodium hydroxide solution containing alcohol. The dark-violet liquid turns pale-red when boiled; on acidifying the solution, *α -benzoylhydrozynaphthaquinone* is deposited in golden plates melting at 220—222°.

β -Benzoylnaphthaquinone melts at 130—132° and the *quinol* at 200° with decomposition. *Anilido- β -benzoylnaphthaquinone* melts at 209—210°, and is almost insoluble in alcohol.

These quinones may be regarded as *α -naphthaquinone*, in which benzoyl, $C_6H_5\cdot CO$, has displaced a hydrogen in the *α -* and *β -* position respectively in that benzene nucleus which does not contain the oxygen-atoms. The *α -quinone* yields a benzoylphthalic acid (m. p. 128°) on oxidation, and the *β -quinone* appears to yield a benzoylphthalic acid melting at 150—151°. W. C. W.

Probable Orthoquinone derived from Anthraquinone. By W. H. RICHARDSON (*Chem. News*, 58, 54—55).—Alkaline solutions of alizarin undergo oxidation readily with the usual agents, but best of all with permanganate or bromine. On acidifying such an oxidised solution, a fawn-coloured precipitate is obtained, which by reduction is reconverted into alizarin. It, moreover, yields dyes with phenylhydrazine; and its sulphonic acid, an anilide with aniline, and its solution reacts easily with orthodiamines. The author assumes that the substance is most likely a quinone or orthodiketone corresponding with alizarin. Further experiments are in progress.

D. A. L.

Essence of Rosewood. By H. MORIN (*J. Pharm.* [5], 18, 17, from *La Nature*, 14th April, 1888).—An essential oil occurs in commerce under the name of *Essence de bois de rose femelle*, which is obtained by the distillation, in the presence of water, of the wood of *Licari kanali* (*Licaria guianensis*) an acroclidium of the Lauracæe order. The essence is limpid, slightly coloured, less dense than water, burns with a smoky flame, and remains liquid at -20°. Its composition is analogous to that of camphor. Distillation of its hydrochloride yields a hydrocarbon, *licarene*, a very mobile, colourless liquid, without action on polarised light, sp. gr. 0.835 at +18°; it has the composition $C_{20}H_{16}$, and consequently is an isomeride of terebenthene.

The odour of the essence recalls that of the rose, mignonette, and orange. J. T.

Shellac. By R. BENEDIKT and F. ULZER (*Monatsh.*, 9, 579—585).—When seedlac (2 kilos.) and sodium carbonate (1 kilo.) are

boiled with water (40 litres) for some time, an oil which solidifies on cooling collects on the surface of the liquid. The wax thus obtained, weighing from 0.5 to 1.0 per cent. of the seedlac taken, has a yellowish-grey colour, and melts at 59–60°. By treatment with alcoholic potash, stearic, palmitic, and oleic acids, together with myricyl and ceryl alcohols, may be isolated: the latter is best separated by heating with acetic anhydride, the resulting acetates being readily separated by fractional crystallisation from alcohol. The wax contains altogether about 50 per cent. of free alcohols.

The authors have proved the presence of resin wax in a sample of commercial shellac examined by them, but are at present unable to say whether or not it is a natural constituent or is simply due to colophony having been melted in with the shellac. G. T. M.

Catalpin. A Bitter Principle. By E. CLAASSEN (*Amer. Chem. J.*, 10, 328–330).—The fruit or bark of *Catalpa bignonioides* is extracted with alcohol, the solution evaporated, the residue dissolved in water, precipitated by lead acetate, the filtrate mixed with barium carbonate, evaporated and extracted with ether-alcohol. The solution evaporated and the residue again dissolved in water. From this solution the catalpin cannot be crystallised except by treating with animal charcoal, filtering, and washing with water, and then extracting the dried charcoal with boiling alcohol; from this solution, the principle separates in silky, acicular crystals. It is a glucoside. Its alcoholic solution is precipitated by addition of chloroform, and from its aqueous solution it is precipitated by basic lead acetate. H. B.

Quercetin. By J. HERZIG (*Monatsh.*, 9, 537–547).—Ethylquercetin is best formed by heating quercetin (12 grams) dissolved in absolute alcohol (300 c.c.) with potash (8 grams) and a corresponding quantity of ethyl iodide for four or five hours in a flask provided with a reflux condenser. The yield is from 62 to 73 per cent. of theory. Ethylquercetin has the characteristic yellow colour of quercetin-derivatives, but when heated with acetic anhydride and sodium acetate gives a colourless acetyl-derivative, crystallising from alcohol in glistening needles melting at 151–153°.

Both ethylquercetin and methylquercetin have a yellow colour, are insoluble in potash, and, therefore, contain no free hydroxyl-groups. In their forming acetyl-derivatives with change of colour, they resemble the quinones. The acetyl-derivatives are decomposed by solution in sulphuric acid: ethylquercetin and methylquercetin respectively being regenerated in theoretical quantity. The author has utilised this property to determine the molecular weight of quercetin, which he finds approaches 292 or perhaps twice that number. G. T. M.

Quercetin-derivatives. By J. HERZIG (*Monatsh.*, 9, 548–561; compare preceding Abstract).—If the molecular weight of quercetin be taken as 584, *rhamnetin* must be regarded as a dimethylquercetin. Treated with methyl iodide and potassium hydroxide, it furnishes a methylrhamnetin identical with the methylquercetin mentioned in the

previous Abstract. This compound is almost insoluble in cold alcohol, but crystallises from a hot solution in beautiful, lustrous, yellow, anhydrous needles melting at 154—155°; and on heating with acetic anhydride and sodium acetate, it yields an acetyl-derivative identical with acetylmethylquercetin. Rhamnetin is readily converted into quercetin by treatment with excess of hydriodic acid. G. T. M.

Rhinanthin. By T. L. PHIPSON (*Chem. News*, **58**, 99).—Leaves and stalks of *Antirrhinum majus* (snap-dragon) are soaked in cold water for a few days, filtered, precipitated with lead acetate, the slight excess of lead acetate is removed from the solution by means of hydrogen sulphide, and the solution evaporated to a thin syrup. After being a few days in a warm, dry place, the syrup deposits rhombic crystals of rhinanthin, which are purified by a second crystallisation from water, and show the properties of rhinanthin obtained from other sources. The author's analyses lead to the formula $C_{64}H_{56}O_{40}$, instead of Ludwig's formula, $C_{58}H_{52}O_{40}$. D. A. L.

Strophantin. By ARNAUD (*Compt. rend.*, **107**, 179—182).—The crushed seeds of *Strophantus kombé* are treated with boiling alcohol of 70° for several hours, and the solution distilled to a small bulk on a water-bath; the distillation is finished in a vacuum, care being taken that the extract remains liquid. The residue is cooled, the supernatant oil and resin separated, the liquid filtered, and heated with a small quantity of basic lead acetate and some finely powdered litharge. The liquid is again filtered, the lead removed by means of hydrogen sulphide, and the filtrate concentrated at 50° to a thick syrup, from which the strophantin slowly crystallises. The crystals may be purified by recrystallisation from boiling water; the yield is 4.5 grams per kilo.

Strophantin is a white bitter substance, which crystallises in micaceous plates, grouped round a nucleus. It readily retains water mechanically, and also forms a hydrate, which loses its water in a vacuum or in dry air. The hydrate melts below 100°, and the residual strophantin is uncrystallisable. If, however, strophantin is carefully dried in a vacuum, it may be heated at 110° without alteration. Anhydrous strophantin becomes pasty at 165°, and partially decomposes. It acts on polarised light: the rotatory power of a 2.3 per cent. aqueous solution $[\alpha]_D = +30^\circ$. It is only slightly soluble in water, and somewhat soluble in alcohol, but is insoluble in ether, carbon bisulphide, and benzene. It is precipitated from its aqueous solutions by tannin.

Strophantiu contains no nitrogen, and has a composition corresponding with the formula $C_{31}H_{48}O_{12}$. It seems to be the immediate higher homologue of ouabain (this vol., p. 848), which it closely resembles in properties. Perhaps these and all other cardiac poisons have a common nucleus. C. H. B.

Diosmin. By P. SPICA (*Gazzetta*, **18**, 1—9).—In the author's former examination of the leaves of *Barosma crenata* and *B. betulina*

(Abstr., 1885, 1142), it was found that after the essential oil had been removed, alcohol extracted from the leaves a crystalline substance, which he called *diosmin*. The amount present in the leaves varies very much, not only with the season when they are gathered, but also with the age of the plant; at no time, however, is it large. The best way of extracting it is first to treat the leaves with light petroleum to remove the essential oil and waxy and resinous matters, then with cold alcohol of 85 per cent., which removes the chlorophyll and acid extractive substances, and finally to treat it with boiling alcohol of 80 to 85 per cent., which is the best solvent for the diosmin. It is very troublesome to purify, but this may be effected by treating the residue left on evaporation of the alcoholic solution successively with a solution of ammonium carbonate, cold alcohol, and ether, and then recrystallising repeatedly from alcohol of 80—85 per cent.

When pure, diosmin is a white, crystalline powder, consisting of very slender microscopic needles, odourless, tasteless, and insoluble in most solvents. Its best solvent is boiling alcohol of 80—85 per cent. It melts at 243—244°, with decomposition and evolution of gas. If cautiously melted on platinum foil, it emits a pleasant odour resembling that of orange peel when it begins to burn; subsequently the odour is like that of caramel. Diosmin does not reduce Fehling's solution. It dissolves in concentrated sulphuric acid, and in solutions of the alkalis with yellow coloration, but at the same time undergoes alteration.

When diosmin is boiled for some time in a reflux apparatus with dilute hydrochloric acid, or with sulphuric acid of 3—4 per cent., it is resolved into a crystalline compound, sparingly soluble in water, and a substance easily soluble in water; the latter has a feeble dextro-rotatory power, and is capable of reducing Fehling's solution. The crystalline substance is moderately soluble in alcohol, and still better in a mixture of alcohol and benzene. It forms minute, orange-yellow needles, for which no definite melting point could be obtained, but it appears to be somewhere about 145°.

The results obtained by the analyses of diosmin dried in a vacuum over sulphuric acid are, $C = 53.43$, $H = 6.17$ (mean of three analyses), which closely agree with the numbers obtained by Paternò and Briosi for hesperidin, namely, 53.44 and 5.92; but E. Hoffman, taking the formula as $C_{22}H_{26}O_{13}$ ($C = 54.77$ and $H = 5.39$), considers that the sample analysed by Paternò and Briosi was incompletely dried, and that a temperature of 150° is necessary to remove all the water.

On heating diosmin in a current of air at 150—160°, it lost 4.2 per cent. of water, and on analysis then gave numbers corresponding with $C = 57.77$ and $H = 6.00$. The author is making a careful comparison of diosmin with hesperidin, in order to ascertain whether they are identical or not.

C. E. G.

Constitution of Quassin. By V. OLIVERI (*Gazzetta*, 17, 570—577).—Of the derivatives of quassin, quassic acid seems to be the compound which is best adapted for investigation, in order to obtain an insight into the constitution of quassin. In order to prepare the

acid, it is advisable to operate on small quantities of quassin at a time (5 grams); this is heated at 100° for one hour in a sealed tube with hydrochloric acid (40 c.c.) diluted with its own volume of water. The solution is separated from resinous matter by filtration, and precipitated with water. The precipitate, after being washed, is crystallised several times from alcohol, by which means the unaltered quassin is easily separated, as the quassic acid is comparatively insoluble in cold alcohol.

Quassic acid, $C_{30}H_{38}O_{10}$, crystallises in small, colourless, monoclinic prisms, containing 1 mol. H_2O , which they lose at 100° . It melts with decomposition about $244-245^{\circ}$, is soluble in boiling alcohol, but only sparingly in cold alcohol and ether. It dissolves in ammonia, and in solutions of alkaline carbonates with a yellow colour, more or less inclined to red. Its ammoniacal solution gives precipitates with mercuric chloride, lead acetate, copper sulphate, and ferric chloride, and reduces silver nitrate; its aqueous solution is coloured greenish-yellow by ferric chloride.

In a previous communication (Abstr., 1885, 907), published by the author in conjunction with Denaro, quassin was regarded as the dimethyl salt of quassic acid. This the author has now confirmed by proving that methyl chloride is formed by the action of hydrochloric acid on quassin, and that quassic acid is bibasic. For this purpose, several of its salts were prepared and analysed. *Barium quassate*, $C_{30}H_{38}O_{10}Ba_2 \cdot 7H_2O$, forms a yellowish-red, crystalline mass. The *lead salt*, $C_{30}H_{38}O_{10}Pb_2 \cdot 6H_2O$, is thrown down as a yellow precipitate, on adding acetate of lead to a neutral solution of ammonium quassate; *ferric quassate*, $(C_{30}H_{38}O_{10})_3Fe_2$, is a brownish-green amorphous precipitate.

On adding a solution of hydroxylamine hydrochloride (6 grams) to quassic acid (10 grams), dissolved in sodium carbonate, an abundant precipitate of the *dioxime of quassic acid*, $C_{28}H_{36}O_8(C:NH)_2$, is thrown down after a little time. It may be purified by crystallisation from alcohol diluted with its own volume of water, when it is obtained in yellowish rectangular prisms; it melts at $228-230^{\circ}$, and is at the same time completely decomposed.

When quassin is heated with concentrated hydriodic acid (sp. gr. 1.70) and some amorphous phosphorus for 20 hours, at a temperature of 150° , gradually increased to 280° , a reducing action takes place, which varies with the temperature; at 150° , methyl iodide is produced, whilst at the higher temperature resinous products and a mixture of hydrocarbons are obtained. The latter, separated from the filtered and neutralised solution by distillation with steam, appeared as a yellowish, oily liquid, which on being submitted to fractional distillation yielded three definite hydrocarbons. The first, boiling at $188-195^{\circ}$, was found to have the composition of β -durene, $C_{10}H_{16}$, and by treatment with bromine yielded a brominated derivative crystallising in colourless needles melting at about 200° . The second fraction, boiling at $220-240^{\circ}$, had the composition $C_{14}H_{18}$, and gave a brominated derivative, which crystallised from alcohol in colourless needles melting at about 150° , and subliming at a lower temperature. The residue which did not come over at 240° , contained anthracene.

The author considers it proved that quassin contains four hydroxyl groups, OH, two carboxymethyl groups, COOMe, and two ketonic groups, CO. From other results obtained, which he hopes soon to publish, it would appear that quassin is an anthraquinone-derivative.

C. E. G.

Jecorin in the Animal Body. By D. BALDI (*Chem. Centr.*, 1888, 978, from *Arch. physiol.*, 1887, Suppl., 100).—The author has obtained jecorin from rabbit's liver, ox spleen, human brain, and horse's muscle, and it appears to constantly accompany lecithin. Next to the liver, the spleen gave the highest yield. Jecorin reduces Fehling's solution, although its reducing power appears to vary with the source from which it is obtained.

J. W. L.

Dye from Seaweed. By F. NETTLEFOLD (*Chem. News*, 58, 15).—By nitrating alginic acid, a light-yellow nitro-product is obtained insoluble in water, but soluble in alkalis to a brown solution. The alkaline, best ammoniacal, solution dyes unmordanted cotton a fine Bismark-brown, fast to soap, excelling many aniline colours, and equalling chrysoidine; the depth of shade is considerable and can be worked to a great intensity. Neither the colour nor the fastness is increased by mordanting with alumina or potassium antimony tartrate. This dye has little affinity for wool, mordanted or unmordanted. In acid solutions it does not dye.

D. A. L.

Pyridine and Piperidine Bases formed from Acetone and Aldehyde-ammonia. By E. DÜRKOFF (*Ber.*, 21, 2713—2718).—When aldehyde-ammonia and acetone are heated together at 200° for 9 to 10 hours, a secondary and tertiary base are obtained, and can be separated by treating the mixture of their hydrochlorides with sodium nitrite. The tertiary base is symmetrical trimethylpyridine; it boils at 167—168°, and yields a copellidine (see below) when reduced with sodium and alcohol. The aurochloride melts at 106° with previous softening (compare Mohler, *Ber.*, 21, 1011). The secondary base is a copellidine, $C_8H_{11}N$. The platinochloride decomposes at 242—244° (compare Jaeckle, this vol., p. 1103).

F. S. K.

Action of Ethyl Acetoacetate on Hexamethylenetetramine. By P. GRIESS and G. HARROW (*Ber.*, 21, 2740—2743).—When a mixture of ethyl acetoacetate (20 grams) and hexamethylenetetramine (4 grams) is heated at 170°, a small quantity of ethyl lutidinedicarboxylate is formed, but the chief product is a yellow, amorphous substance; if, however, chloride of zinc (20 grams) is added, only small quantities of the amorphous substance are formed, and considerable quantities of ethyl lutidinedicarboxylate (compare Engelmann, *Abstr.*, 1886, 259) and ethyl hydrolutidinedicarboxylate are produced.

Ethyl hydrolutidinedicarboxylate, $C_6NH_3Me_2COOEt$, separates almost completely when the product of the reaction is mixed with hot water, the cold solution filtered, and the residue extracted with boiling alcohol. It crystallises in anhydrous needles or in greenish-yellow, quadratic plates, melts at 170° with previous softening, and is readily

soluble in chloroform, but only very sparingly in cold alcohol and ether, and almost insoluble in boiling water. It has a neutral reaction, and distils with considerable decomposition. When treated with nitrous acid in alcoholic solution, or when dissolved in hot, dilute hydrochloric acid, it is converted into diethyl lutidinedicarboxylate, melting at 72° , but in the latter reaction, as a rule, a considerable quantity of monethyl lutidinedicarboxylate, $\text{COOH}\cdot\text{C}_6\text{NHMe}_2\cdot\text{COOEt}$ (compare Weiss, Abstr., 1886, 719) is also formed.

F. S. K.

Constitution of the Parvoline obtained from Propionaldehyde-ammonia and Paraldehyde. By E. DÜRKOPF and M. SCHLAUGK (*Ber.*, 21, 2707—2708).—The pyridinecarboxylic acid which the authors obtained by oxidising parvoline (compare this vol., p. 607) is identical with carbodinicotinic acid (Weber, Abstr., 1887, 1117). It melts at 315° as the average of several observations, crystallises with 2 mols. H_2O , and is converted into dinicotinic acid when heated at 150° .

F. S. K.

Piperidine Dyes. By B. LACHOWICZ (*Monatsh.*, 9, 505—509).—When piperidine is added to quinone dissolved in alcohol, a reddish-brown solution is obtained, from which a dye, *dipiperylquinone*, $\text{C}_6\text{H}_2\text{O}_2(\text{C}_5\text{H}_{10}\text{N})_2$, separates in thick, reddish-violet prisms. It melts at 178° , is insoluble in water, but dissolves in alcohol and dilute hydrochloric acid. Its mode of formation is shown by the equation $3\text{C}_6\text{H}_4\text{O}_2 + 2\text{C}_5\text{H}_{11}\text{N} = \text{C}_6\text{H}_2\text{O}_2(\text{C}_5\text{H}_{10}\text{N})_2 + 2\text{C}_6\text{H}_4(\text{OH})_2$. Digestion with strong hydrochloric acid converts it into dihydroxyquinone and piperidine hydrochloride.

Dipiperylquinone is analogous in constitution to the compound obtained by Mylius (Abstr., 1885, 804) from the interaction of dimethylamine and quinone, but the mode of formation is altogether different; in the latter case, oxidation is brought about by atmospheric oxygen, whereas in the production of dipiperylquinone by the above method oxidation takes place at the expense of a portion of the quinone present. Dipiperylquinone may, however, be readily obtained by a process identical with that used by Mylius, namely, by exposing mixtures of quinol and piperidine to the action of atmospheric oxygen. Piperidine forms dyes with toluquinone, naphthaquinone, and phenanthraquinone, but the reaction does not take place nearly so readily as with quinone, nor has the author yet been able to obtain the compounds in a pure condition.

G. T. M.

Furfurethenepyridine. By E. MERCK (*Ber.*, 21, 2709—2712).—*Furfurethenepyridine*, $\begin{smallmatrix} \text{CH}\cdot\text{CH} \\ \text{CH}\cdot\text{O} \end{smallmatrix} \rightarrow \text{C}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_5\text{NH}_4$, is formed when a mixture of furfuraldehyde and α -picoline is heated at 160 — 170° with a small quantity of zinc chloride. The yield is about 10 per cent. of the picoline employed. It crystallises from water in white needles, quickly blackens on exposure to the air, and is readily soluble in alcohol and ether, but almost insoluble in water. The freshly distilled base has a slight but characteristic odour, and melts at 51 — 53° . The *mercuriochloride*, $\text{C}_{11}\text{H}_9\text{NO}\cdot\text{HgCl}_2$, crystallises in yellow needles,

and melts at 133°. The *platinochloride*, $(C_{11}H_9NO)_2, H_2PtCl_6 + 2H_2O$, crystallises in microscopic, reddish-yellow needles melting at 155° with decomposition. The *picrate*, $C_{11}H_9NO, C_6H_3N_3O_7$, crystallises in yellow needles and melts at 185—190°. The *aurochloride* is reddish-brown.

Furfurethanepiperidine, $\langle \begin{smallmatrix} CH \cdot CH \\ CH \cdot O \end{smallmatrix} \rangle \cdot C \cdot CH_2 \cdot CH_2 \cdot C_5H_{10}N$, obtained by reducing the preceding compound with sodium and alcohol, is a strongly alkaline liquid with a marked piperidine-like odour. It boils at 245—247°. The *hydrochloride*, $C_{11}H_{17}NO, HCl$, melting at 145—148°, the *hydrobromide*, melting at 133—135°, and the *hydriodide*, melting at 119—121°, are crystalline. The base is a powerful poison.

F. S. K.

Alkaloids from Cod-liver Oil. By A. GAUTIER and L. MOURGUES (*Compt. rend.*, 107, 110—112, and 254—257).—Pale or fawn-coloured oil from Norway or Sweden is treated with its own volume of alcohol of 33° containing 4 grams of oxalic acid per litre. The alcohol is separated, saturated almost exactly with calcium oxide, filtered, and distilled in a vacuum at 45°. The product is digested with calcium carbonate, neutralised with lime-water, evaporated to dryness in a vacuum, and the residue extracted with alcohol of 90°. The alkaloids are purified in the usual manner; the yield is 0.35 to 0.5 gram per kilo.

The fraction boiling at 87—90° consists of butylamine; at 96—98°, amylamine; just below 100°, hexylamine; at 198—200°, a new base, *hydrolutidine*. The non-volatile residue contains a new base, *aselline*, the hydrochloride of which is insoluble, and a second, *morruine*, which forms a soluble, crystallisable platinochloride. Cod-liver oil also contains a small quantity of lecithin and a peculiar crystallisable nitrogenous acid, *gaduinic acid*.

Butylamine has distinct toxic properties, and in small doses increases the activity of the functions of the skin and the kidneys. Larger quantities produce fatigue, stupor, and vomiting. The isoamylamine, which constitutes about one-third of the total volatile bases, is identical with the isoamylamine obtained by the action of potassium hydroxide on isoamylcarbimide. It exerts a powerful physiological action, 4 mgrms. of the hydrochloride having killed a greenfinch in three minutes. In small doses, it excites reflex action, and the urinary secretions; in large doses, it produces general tremor, well-marked convulsions, and death. Hexylamine, which is present in very much lower proportion, produces similar effects but is much less powerfully toxic.

The fraction of the bases which boils at 198—200° under a pressure of 770 mm. consists of *dihydrolutidine*, $C_7H_{11}N$, a colourless, oily, strongly alkaline and caustic liquid; it boils at 199° under normal pressure, and its vapour-density at 299° = 3.3. When exposed to air it absorbs carbonic anhydride, becomes viscous, and darkens in colour. The hydrochloride crystallises in confused needles which seem to belong to the rhombic system. The nitrate, like the nitrates of hydropyridic bases, reduces a solution of silver nitrate. The sulphate crystallises in stellate groups of deliquescent needles. All these salts

have a bitter taste. The platinochloride is only slightly soluble, and crystallises from a hot solution in canary-yellow lozenge-shaped lamellæ. When boiled with a large quantity of water, it loses hydrogen chloride, and is converted into a modified salt, $(C_7H_{11}NCl)_2PtCl_2$, which is much less soluble than the original compound, and forms confused crystals of a paler colour. The aurochloride crystallises in needles or plates, and is somewhat stable even when heated.

The methiodide forms readily at the ordinary temperature with development of heat, and crystallises in colourless needles which dissolve in water or alcohol, and have a disagreeable and somewhat nauseous odour. With potassium hydroxide, it yields dihydromethylutidine, a colourless, strongly alkaline aromatic oil. When dihydrolutidine is boiled with potassium permanganate, an aromatic odour resembling that of coumarin is observed, and this points to the intermediate formation of a compound containing the aldehyde-group. Oxidation is completed in a sealed tube at 100° , and the product is methylpyridinecarboxylic acid, $C_5NH_3Me\cdot COOH$. It follows that the dihydrolutidine is dihydrodimethylpyridine, $C_5NH_3Me_2$.

Dihydrolutidine is moderately poisonous, and in small doses reduces the general sensibility. Larger doses produce tremor, especially of the head; depression, with alternating periods of intense excitement and paralysis of the lower members, ending in death.

C. H. B.

Narcotine. (Part II.) By W. ROSER (*Annalen*, **247**, 167—177).—Methyl iodide unites with narcotine, forming narcotine methiodide, an oily liquid. Narcotine metho-chloride and the platinochloride are crystalline. On the addition of sodium hydroxide to narcotine metho-chloride, narcotine methyl hydroxide is precipitated, but this compound soon changes into pseudonarcaine, $C_{23}H_{27}NO_8$, and the transformation is greatly facilitated by exposure to steam. A careful examination of pseudonarcaine and its derivatives brings the author to the conclusion that this substance is identical with narcaine. The formation of pseudonarcaine from narcotine methyl hydroxide is represented by the following equation: $C_{22}H_{23}NO_7\cdot CH_3\cdot OH + 3H_2O = C_{23}H_{27}NO_8\cdot 3H_2O$.

W. C. W.

Conversion of Hyoscyamine into Atropine by Bases.
Action of Mass. By W. WILL and G. BREDIG (*Ber.*, **21**, 2777—2797; compare Will, this vol., p. 855).—The authors investigated the action of soda on a solution of hyoscyamine containing 6.6667 grams in 100 c.c., and on a solution of twice this concentration. The results, which are given in tabular and diagrammatic form, show that in the same time the rotatory power of the more concentrated solution is diminished twice as much as that of the more dilute solution. The action of the soda is, therefore, a catalytic action.

Tables are also given showing that to produce a certain decrease in the rotatory power of a solution containing a given quantity of hyoscyamine, a definite volume of normal soda takes four times as long as the same volume of a solution containing four times as much soda. The results obtained with dimethylamine show that the action of this base is quite similar to that of soda.

The decrease in the rotatory power of solutions containing the same quantity of hyoscyamine, under the influence of soda, potash, tetramethylammonium hydroxide, dimethylamine, and ammonia, of different concentrations, is given in tabular form, and shows that ammonia and dimethylamine act much more slowly than the other three bases.

From the observed final rotatory power of solutions of hyoscyamine under the influence of soda, potash, and tetramethylammonium hydroxide, based on the assumption that the hyoscyamine has been completely converted into atropine, the specific rotatory power of the latter is $[\alpha]_D = -1.89$.

When the conversion of hyoscyamine into atropine is almost complete, a small quantity of the latter is decomposed into tropine and tropic acid; owing to this secondary reaction the relative values of the velocity constants are increased in the case of soda, potash, and tetramethylammonium hydroxide, and decreased in the case of ammonia and dimethylamine.

The authors intend to try and measure the action constants of bases by a more complete study of this phenomenon. Sodium carbonate converts hyoscyamine into atropine, but ammonia has the slowest action of all the bases experimented with.

F. S. K.

Tetanine and Mytilotoxine. By L. BRIEGER (*Chem. Centr.*, 1888, 1007, from *Arch. pathol. Anat.*, 112, 549—551).—The hydrochlorides of these bases decompose gradually, and lose their toxic properties. The product of decomposition of the tetanine hydrochloride gave a platinochloride of the formula $C_6H_{13}NO_2, H_2PtCl_6$. Mytilotoxine is best preserved in the form of aurochloride.

J. W. L.

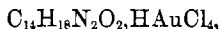
Anagyryne. By E. HARDY and N. GALLOIS (*Compt. rend.*, 107, 247—249).—The authors discovered anagyryne in 1885 (*Compt. rend. Soc. Biol.*, 1885, 391) two years before Reale's description of the alkaloid (*Gazzetta*, 1887, 385).

The seeds of *Anagyris foetida* are macerated with cold water, treated with basic lead acetate, the lead removed by hydrogen sulphide, and the filtrate concentrated and mixed with mercuric chloride, which precipitates the anagyryne. The precipitate is decomposed by hydrogen sulphide, and the concentrated filtrate saturated with sodium carbonate and agitated with chloroform, the chloroform solution being afterwards agitated with hydrochloric acid, from which the hydrochloride crystallises on evaporation.

Anagyryne, $C_{14}H_{18}N_2O_2$, is a yellowish, amorphous substance which dissolves in water, alcohol, or ether, and softens and becomes viscous when exposed to the air. Its solutions give a white precipitate with potassium mercuriodide, a brown precipitate with iodine solution, and the usual general reactions for alkaloids. With acids, it forms salts which, contrary to the statement of Reale, crystallise readily.

Anagyryne hydrochloride, $C_{14}H_{18}N_2O_2, HCl + 4H_2O$, forms white, rectangular tables belonging to the rhombic system, does not alter when exposed to air, and dissolves very readily in water or chloroform,

but is less soluble in alcohol, and only slightly soluble in ether. The crystals become anhydrous at 125° . The rotatory power of the hydrochloride is $[\alpha]_D = -114^{\circ}$. The *aurochloride*,



forms at first a yellow, amorphous precipitate, but this rapidly becomes crystalline. The *platinochloride*, $C_{14}H_{18}N_2O_2 \cdot H_2PtCl_6$, separates in crystalline tufts. All these salts were analysed, and the composition of the alkaloid was thus definitely determined.

Anagryne has a moderate toxic action. In warm-blooded animals it produces vomiting, coldness, and tremor, slackening of the respiratory movements, and finally stoppage of respiration and circulation. When administered to a frog, the abolition of muscular movements is very remarkable; the motions of the heart persist long after all other movements have ceased.

C. H. B.

Constitution of Spongin. By P. ZALOCOSTAS (*Compt. rend.*, 107, 252—254).—The organic matter of sponges, previously treated with hydrochloric acid and with benzene, was heated in sealed tubes with a solution of barium hydroxide as in Schutzenberger's experiments with proteïds. The products are ammonia, carbonic anhydride, acetic acid, oxalic acid, and a mixture of solid nitrogenous bases, namely, leucine, butalanine, glycalanine, traces of tyrosin, and a hydroproteic acid or hydrate of leucine. The ammoniacal nitrogen is equivalent to one-fourth of the total nitrogen, and 2 mols. of ammonia are formed for each molecule of carbonic anhydride. The number of molecules of water assimilated is equivalent to the number of atoms of nitrogen in the original compound. In the solid products, the ratio of carbon-atoms to hydrogen-atoms is 1 : 2, and that of nitrogen to oxygen 1 : 2.66. It follows from these results that spongin is closely related to the collagenous proteïds.

C. H. B.

Peptonic Fermentation of Meat. By V. MARCANO (*Compt. rend.*, 107, 117—119).—If chopped flesh is mixed with the juice and tissues of the *agave* or American aloe, the solution of the fibrin is complete in five to six hours, and the yield of peptone is about 20 per cent. (Compare Abstr., 1885, 181.) If the chopped and squeezed flesh is mixed with the tissues and juice of the plant without addition of water and kept at 35° , it swells up, but little peptone is formed. The magma thus produced is mixed with water and heated to 70° , when it liquefies immediately and yields a highly concentrated solution of peptone. It would seem that a pepsin is formed and unites with the fibrin, producing a compound which is insoluble at 35° but dissolves readily in water at 70° .

Equal quantities of flesh were mixed with fresh agave tissue and with some of the same tissue after boiling with water. The formation of peptone was much greater in the first case, and hence it follows that the peptonising power resides mainly in the living vegetable cell.

This process is employed successfully on a large scale for the manufacture of peptone.

C. H. B.

Physiological Chemistry.

Feeding of Calves and Pigs. By N. J. FJORD (*Bied. Centr.*, 1888, 590—601).—Experiments made with calves and pigs on the relative value of skim-milk obtained by centrifugal separators and by the Holstein tub method, the former containing 0.15 per cent. of fat and the latter 0.6 per cent., showed that the latter kind gave a slightly larger increase in weight in a given time, but that the money value of this increase was only about one-fifth of that of the butter fat sacrificed.

Some experiments with pigs on the relative feeding values of corn, skim-milk, and whey, and on other points, led to the following conclusions:—

1. The opinion that pigs make better use of their food when it is largely diluted with water was not confirmed; the differences in increase obtained being either unimportant or to the disadvantage of dilution.
2. Although confining pigs produced more increase than allowing them to run in the sty-yard, yet the author thinks it may cause disease.
3. 12 parts by weight of whey, 6 parts of skim-milk, 1 part of bruised barley, and 1 part of bruised rye are of approximately equal feeding value.

These conclusions were deduced from the average increase in weight in equal times. In the experiments for conclusion 3, on slaughtering the pigs the amount of offal and the thickness of the fat were determined, and the pigs were classified by experts according to their quality, and the results bore out fairly well the statement given above.

H. Nathorst, remarking on the above experiments, states that the equivalency of the foods mentioned is not of universal application (as Fjord too observes), for the substitution of one food for another may materially alter the albuminoid ratio of the diet. H. H. R.

Influence of Fodder on the Production of Lean and Fat in Pigs. By HENRY (*Bied. Centr.*, 1888, 606—609).—Six pigs of 100 days old, and from the same litter, were selected and divided into two equal lots. Set I received a diet of 1 part by weight of dried blood, 6 parts of bran, and 14 parts of skim-milk. Set II received an unlimited amount of maize meal. The albuminoid ratio of the diet of set I was 1 : 2, and of that of set 2 was 1 : 7 or 8. At the end of 136 days from the commencement of the experiment, the pigs were slaughtered and the weights of different parts were determined. The weights obtained for set I in every case, except as regards fat, exceeded those for set II; the live weights were 19 per cent. greater for set I than for set II, the carcasses 21, the kidneys 42, the spleens 33, the livers 32, the blood 59, the hair and skins 36, the large muscles of the back (*Ilia spinalis*) 64, the two muscles of the body cavity (*Psoas magnus*) 38, and the bones 23 per cent. greater. In set I, 38 per cent. of the bodies, excluding bones, was fat; in set II

46 per cent. of fat was present. The strength of the thigh bones was determined by a specially constructed machine, and was found to be 62 per cent. greater for set I than for set II. From these results the author infers that by varying the feeding, fat or lean can be produced at will, and also that feeding exclusively with maize or other foods over rich in carbohydrates affects the whole organism unfavourably, and so may be dangerous if the animals are used for breeding.

H. H. R.

Cutaneous Excretion of Albumin by the Horse. By A. LECLERC (*Compt. rend.*, 107, 123—126).—The white secretion frequently observed on a horse which has perspired, yields an opalescent solution, which always contains albumin, alkaline chlorides, ammonium salts, urea, and one or more nitrogenous organic compounds. On four consecutive days, a horse which perspired freely excreted 10·308, 5·558, 4·237, and 5·596 grams of albumin respectively. Another horse, which perspired much less readily, excreted on four consecutive days 8·605, 2·701, 2·690, and 4·114 grams of albumin. It is evident that the loss of albuminoid and other nitrogen in this manner must be taken into account in all considerations of the circulation of nitrogen.

The dried perspiration forms a white deposit which has usually been regarded as epithelial *débris*. The latter, however, is present in very small proportion, and the substance consists mainly of salts and albumin which is still completely soluble in water.

C. H. B.

Mean Composition of Normal Urine. By YVON and BERLIOZ (*Lancet*, 2, 1888, 629, from *Rev. Méd.*, 8, 713—718).—A series of tables of the analysis of normal urine are given. The observations are very numerous, and were made on healthy adults, male and female. The present results are contrasted with those of other authors, and in each case the maxima and minima as well as the means are given. The latter are summarised thus:—

	Male.	Female.
Volume per diem	1360 c.c.	1100 c.c.
Specific gravity	1·0225	1·0215
Urea (per litre)	21·5 gram	19·0 gram
„ (per diem)	26·5 „	20·5 „
Uric acid (per litre)	0·5 „	0·55 „
„ (per diem)	0·6 „	0·57 „
Phosphoric acid (per litre)	2·5 „	2·4 „
„ (per diem)	3·2 „	2·6 „

Thus, with the exception of uric acid, the amounts are higher on each head among males than among females; but with uric acid, the quantities eliminated in the 24 hours are almost precisely the same for the two sexes. The authors desire to correct, as resulting from these observations, the proportionate quantities of urea and uric acid given in their *Manual of Urinary Analysis*, which should be as 40 : 1 instead of 30 : 1, and of urea and phosphoric acid, which should be as 8 : 1 instead of 10 : 1.

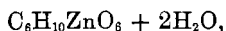
W. D. H.

Secretion of Urine when Pressure is exerted on the Urinary Canals. By R. LÉPINE and E. PORTERET (*Compt. rend.*, 107, 74—77).—The experiments were made with dogs. A canula was placed in each ureter, and from one of these the urine was allowed to escape freely, the other being attached to an india-rubber tube. In the second case, the urine escaped from the free end of the tube, and by raising this, a back pressure was produced by the accumulation of urine in the tube, the pressure being measured of course by the height of the column of liquid. By operating in this manner, it was possible to collect and analyse the urine secreted at the same time by each kidney, the one being under pressure whilst the other was under normal conditions.

The quantity of urine secreted under pressure varies greatly in different animals. In some cases, the secretion is almost stopped, whilst in others it is only slightly reduced. In these experiments, the secretion was accelerated by the intra-venous injection of a 5 per cent. solution of sodium chloride. The quantity of urine secreted has no relation to the pressure. Under feeble pressure; it would seem that the quantity of urea diminishes in somewhat greater proportion than the volume of urine, whilst with a pressure of 45 cm. the volume of urine diminishes to a much greater extent than the quantity of urea. As a rule, the inorganic salts vary in the same ratio as the volume of urine, but under feeble pressure the ratio of chlorides is higher than that of other salts, whilst under higher pressure the reverse is the case. The proportion of phosphates also diminishes under pressure. When sugar is injected into the veins, the quantity in the urine varies directly as the volume of the latter. The urine excreted under pressure is really the resultant of a double process of secretion and resorption.

C. H. B.

Paralactic Acid in the Urine of Soldiers after a Forced March. By G. COLASANTI and R. MOSCATELLI (*Gazzetta*, 17, 548—557).—Although it has long been known that the ordinary optically inactive lactic acid occurs in urine both normal and pathological, the presence of paralactic acid, the other ethylidenelactic acid, in normal urine has never been decisively proved; it has, however, been stated to exist in some pathological urines. The author has operated on comparatively large quantities of fresh urine collected after forced marches of 20 to 25 kilometres, and has conclusively proved the presence of paralactic acid in it. The urine, as soon as collected, was evaporated on the water-bath to a syrupy consistence, and the acid converted into the zinc salt by treatment with zinc carbonate in the way recommended by Salkowski. The crude zinc salt was repeatedly washed with absolute alcohol, to remove a brown resinous substance, and then repeatedly crystallised. By spontaneous evaporation, it was obtained as a mass of colourless, brilliant, microscopic, prismatic crystals of the composition of zinc paralactate,



agreeing in all its properties with the salt described by Wislicenus.

This proves beyond doubt that the acid which Du Bois Reymond

has shown to be produced in muscle when in activity enters into the circulation; a part is oxidised to carbonic anhydride and water, as Spiro has recently proved experimentally, and a part passes through the kidneys unaltered, and is excreted with the urine.

C. E. G.

Behaviour of Urine after Ingestion of Naphthalene. By EDLEFSEN (*Chem. Centr.*, 1888, 1007, from *Centr. Klin. Med.*, 9, Beil., 90—92).—Fresh urine after the use of naphthalene, gives a blue fluorescence when treated with ammonia or soda. When treated with bleaching powder and hydrochloric acid, it gives the red β -naphthoquinone reaction. Fischer's reaction with diazoamidobenzene also shows the presence of β -naphthol. The urine becomes cherry-red on standing for several days with acetic acid. Under these latter circumstances, the phenol test may also be successfully applied.

J. W. L.

Excretion of Uric Acid. By A. HAIG (*J. Physiol.*, 8, 211—217, *Medico-Chirurg. Trans.*, 71, 125—138, and 283—295).—The administration of acids diminishes the relative amount of uric acid excreted, and that of alkalis increases it: as an instance, in one case the normal proportion of uric acid to urea was 1:35. After a few doses of 4 grams of citric acid, the relation was 1:41; after similar doses of potassium citrate, it was 1:28. In these cases, there is not only a relative, but also an absolute diminution and increase in the uric acid excreted. The excretion of uric acid is much affected by the digestion of food, and is three times as much during the "alkaline tide" as at other periods: a large part of this increased secretion must be regarded as a washing out of the uric acid accumulated in the liver and spleen in the "acid tide" periods between meals, or during sleep, and not as entirely due to increased formation of uric acid during digestion. Certain peculiar forms of headache most marked during the strongest "alkaline tide" as during the digestion of breakfast, are regarded as being due to the increased amount of uric acid in the circulation during that period. Such headaches may be cured by a dose of acid.

Salicylic acid, however, forms an important exception to this rule, for while it increases urinary activity it does not in any way diminish the excretion of uric acid; moreover, acids given while salicylates are present in the circulation have no longer the power of diminishing the excretion of uric acid; excessive excretion of uric acid under salicylates is not accompanied by any headache. Benzoates do not act in the same way, probably because hippuric acid which they form is less soluble than salicyluric acid. Both uric and salicyluric acids are present in the urine passed under the influence of salicylates; this is probably due to the salicylate acting on the uric acid in the blood, but not on that secreted by the kidney itself. In these experiments, Haycraft's method of estimating uric acid was employed. Salicyluric acid does not give the reactions on which this process depends.

A large part of the value of salicylates in uric acid diseases is due to their preventing acids from causing retention of uric acid. Some

drugs have the opposite action, and cause retention of uric acid. Lead, iron, and lithia are instances of these. The action of lead in precipitating an attack of gout is well known. Iron also causes relapses in gout and does harm in epilepsy and uric acid headache. On the other hand, salicylates prevent gout, the peculiar headache in question, and also epilepsy. This and certain other facts not chemical in nature seem to place epilepsy in the same category as gout, and it is considered probable that epilepsy is really an uric acid disease, the poison (uric acid) acting on the nerve-centres.

W. D. H.

Lactic Acid in the Urine of Cold-blooded Animals after Extirpation of the Liver. By E. NEBELTHAU (*Zeit. Biol.*, **25**, 123—136).—Minkowski (*Arch. Exp. Path. Pharm.*, **21**, 41) has shown that lactic acid is present in the urine of geese from which the liver has been removed, and absent in the urine of healthy geese. Marcuse has investigated the question whether the same holds true for the cold-blooded animals (*Pflüger's Archiv*, **39**, 425); he found in the case of frogs that it did. He used as a test for lactic acid Uffelmann's colour reaction with ferric chloride (*Zeit. klin. Med.*, **8**, 392); he also found that the calcium salt prepared from the acid had a percentage of water of crystallisation corresponding with that of calcium lactate. Marcuse's experiments not being considered satisfactory, from the small quantity of material he worked with, and Uffelmann's test being not wholly characteristic of lactic acid, the present research was undertaken. Preliminary experiments with tortoises proved negative, as these animals secreted no urine after the operation. Frogs were then taken. Some hundreds were kept in a tank, in water; the increase in the volume of the water was taken as being due to the urine of these animals. The urine thus took several weeks to collect, and putrefaction was prevented by the use of a small quantity of corrosive sublimate. The liver was then removed, and the urine similarly collected; by this method many litres of frog's urine was obtained.

The following are the chief analytical facts ascertained with regard to the urine before and after the operation:—

	Before operation.	After operation.
Specific gravity.....	1·0015	1·0025
Reaction.....	faintly acid	less acid
Total solids.....	0·1062 per cent.	0·140 per cent.
Ammonia.....	0·0054	„ 0·0122 „
Chlorides.....	} present	present
Sulphates.....		
Phosphates.....		
Uric acid.....	absent	absent
Urea.....	present	absent
Lactic acid.....	absent	absent

The method adopted in the case of lactic acid was to attempt to prepare zinc lactate; none was obtainable in either case. The experiment was repeated using a different method of collecting the urine;

this time it was simply squeezed several times daily from the bladder of the animals. In this way, nearly 8 litres were obtained (by the previous method only 3 litres were obtained between the operation and the death of the animals). From this quantity collected after the operation of removal of the liver, 0.1279 gram of a zinc salt was obtained, which in two of its properties resembled paralactate of zinc, namely, in the yellow colour it gave with ferric chloride, and in the lævorotatory action of its solution, on polarised light. The quantity obtained was insufficient to make trustworthy estimations of water of crystallisation, and the crystalline form of the substance gave no very conclusive evidence. W. D. H.

Thiocyanic Acid in the Animal Organism. By J. BRUYLANTS (*J. Pharm.* [5], 18, 104—107, 153—156). The identification of thiocyanic acid was based on the following facts: When an aqueous solution of the above compound is treated with an excess of hydrochloric acid and with ether, the thiocyanic acid passes completely into the ether without decomposition, provided not too much be present. When a thiocyanate is distilled with an excess of a strong mineral acid, most of the thiocyanic acid passes over with the first portions of the distillate. In saliva from healthy subjects, the amount found corresponded to 0.0963 gram of ammonium thiocyanate per litre. Human urine averaged 0.0027 gram per litre, about one-tenth of the amount admitted by Gscheidlen, and one-fortieth of the average proposed by Munk. There appears to be no definite relation between the amount found in saliva and the amount found in urine. Horse's urine contains a little more than human urine. Cow's urine averages 0.0042 gram per litre. Defibrinated cow's blood contained 0.00075 gram per litre. Serum from cow's blood gave 0.0009 gram; and dried albumin contained 0.0095 gram per kilo. Cow's bile contained 0.01 gram per litre. Three samples of cow's milk gave respectively 0.0008, 0.0024, 0.0016 gram per litre. The foregoing results show that thiocyanic acid is found not only in saliva, but in most, if not all, physiological and pathological fluids. It is difficult to think that this compound is formed exclusively in the saliva, since in some individuals this secretion has only contained traces, whilst the urine contained relatively large amounts. J. T.

Blood Changes in Disease. P. W. LATHAM (*Lancet*, 2, 1888, 751—756).—This address constituted the Harveian oration for the present year, and will be found to contain many suggestions of interest both to the chemist and biologist. Among other points, it is shown how it is possible to obtain certain of the poisonous alkaloids or ptomaines, on the supposition that the author's theory of the constitution of albumin is correct. (Abstr., 1886, 635.) W. D. H.

Pernicious Anæmia. By W. HUNTER (*Lancet*, 2, 1888, 555—559, 608—611, 654—648). In an elaborate research, clinical, microscopical, and chemical, into the pathology of the obscure disease known as pernicious anæmia, the following conclusions are drawn:—The essential pathological feature is an excessive destruction of the microscopic

elements of the blood, not an insufficient formation of these. The most constant change is a large excess of iron in the liver, which at once distinguishes pernicious anæmia post mortem from all other varieties of anæmia. The destruction of the blood differs both in its nature and seat from that found in malaria, and in various forms of hæmoglobinuria. The view can no longer be held that the occurrence of hæmoglobin in the urine simply depends on the quantity of hæmoglobin set free; on the contrary, the *seat* of the destruction and the *form* assumed by the hæmoglobin when liberated are important conditions regulating the presence or absence of that substance in the urine, in any case in which an excessive disintegration of corpuscles has occurred. In paroxysmal hæmoglobinuria, such disintegration occurs in the general circulation, and is due to a rapid dissolution of the red corpuscles. In pernicious anæmia, however, the seat of the destruction is chiefly the portal circulation, more especially that portion of it contained within the spleen and the liver, and the destruction is effected by the action of certain poisonous agents of a cadaveric nature absorbed from the intestinal tract. W. D. H.

Physiological Action of Iron. By SKVORTZOFF (*Brit. Med. Jour.*, 2, 1888, 727, from *Vratsch*, 1888, 561).—This is a preliminary note giving the results of experiments on dogs, carried out with the view of determining the action of iron on nitrogenous metabolism in a healthy organism. The following are the conclusions:—(1.) Iron has no marked influence on the nitrogenous metamorphosis in a healthy system. (2.) On the internal administration of iron in daily doses, over 0·02 to 0·03 gram, the assimilation of the nitrogenous ingredients of the food decreases, although but slightly (from 98·4 per cent. before the experiment to 97 per cent. during it). (3.) After venesection, the assimilation somewhat increases, both on the administration of iron and without it. (4.) On the administration of iron with food after venesection, the restoration of hæmoglobin proceeds more rapidly than without iron. (5.) The same holds true in regard to the body's weight. W. D. H.

Physiological Action of Ulexine. J. R. BRADFORD (*J. Physiol.*, 8, 79—85).—Ulexine is an alkaloïd originally prepared by Gerrard from the seeds of the common gorse (*Ulex Europæus*). The hydrobromide was used, since this salt crystallises more readily than any other, and so may be obtained in a greater degree of purity. It was found to have a powerful and wide-spread action, being a nerve and muscle poison, a respiratory poison raising arterial tension, and producing diuresis. The paralysis of respiration is produced by the smallest doses, and is apparently the most important action of the drug. W. D. H.

Albumose, Peptone, and Neurine as Pyrexial Agents. By I. OTT and C. COLLMAR (*J. Physiol.*, 8, 218—228).—The various albumoses as prepared by Kühne and Chittenden, peptone, papain (probably from the fact that it consists largely of an albumose), neurine, and commercial trypsin (which also contains products of

digestion), all cause in cats and rabbits a rise of temperature or fever. Calorimetric observations show also an increase in heat production. The fever reaches its height about two hours after the injection of the substance into the jugular vein. This, however, does not occur in curarised animals. Pflüger has shown that curare paralyses the thermic nerve-fibres, and so the action of these substances is probably primarily on the nervous system.

W. D. H.

Toxic Effects of Albuminous Urine. By J. TEISSIER and G. ROQUE (*Compt. rend.*, 107, 272—275).—In some cases, an increase in the toxic effect of urine affords valuable evidence of increased gravity in the condition of the patient, but this does not always hold good, especially in cases of nephritis. Albuminous urine secreted during sleep is more poisonous than that secreted when awake, whilst with normal urine the reverse is true. In some cases, the toxic effect is in proportion to the quantity of albumin present, but in other cases there is no relation of this kind. No definite connection could be traced between the general composition of the urine and its toxic action.

C. H. B.

Toxic Action of Ouabain and Strophantin. By E. GLEY (*Compt. rend.*, 107, 348—351).—The characteristic effect of both substances is the rapid effect on the heart of a frog which is arrested in systole. 0.025 of a milligram of ouabain produces this effect in six minutes, whilst the same quantity of strophantin requires 12 minutes. With 0.012 milligram of ouabain, the arrest takes place in nine minutes. To the rabbit, ouabain is twice as poisonous as strophantin, to a dog three times, to a guinea-pig four times. Moreover, strophantin is always less rapid in its action. Both compounds act less energetically when introduced into the stomach than when injected into the veins.

C. H. B.

Preventive Inoculation of Rattlesnake Venom. By H. SEWALL (*J. Physiol.*, 8, 203—210).—Repeated inoculation of pigeons with sub-lethal doses of rattlesnake venom (which has been shown by previous observers to be proteid in nature, see Abstr., 1886, 1057) produces a continually increasing resistance towards the injurious effects of the poison without any apparent influence on the general health of the animals. The efficiency of resistance against the venom gradually fails in the absence of fresh inoculation. In some cases, however, the prophylactic effect of the repeated inoculations was persistent for a period of five months.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

A Ferment from Putrefactive Bacteria which Dissolves Fibrin. By E. SALKOWSKI (*Zeit. Biol.*, **25**, 92—101).—Fibrin, which had been well washed and exposed for a few days to a temperature of

7—10°, was then kept for many months under chloroform-water (5 c.c. of chloroform to a litre of water), and examined at intervals of every few months. By this means, putrefaction was entirely prevented. The fibrin, however, entered slowly into solution; the proteïds in solution were at first globulin and albumin; later on, these diminished, and albumoses and ultimately peptones appeared.

The different albumoses of Kühne and Chittenden were separated, and full details relating to heat coagulation, precipitation by neutral salts, &c., are given of the various proteïds discovered from time to time. By the end of seven months, at the ordinary atmospheric temperature, there was but little undissolved residue, and that was of a glutinous nature.

The question arises, what is the source of the ferment which brings about this action? It is certainly an unorganised ferment, as living bacteria were excluded throughout the experiment. The ferment must either have been derived from the blood from which the fibrin was obtained, or from the bacteria which contaminated the fibrin after the process of washing.

In order to settle the question, fibrin was first well washed, part was heated in a current of steam, and then put into chloroform-water, the rest was put into chloroform-water directly. In neither case was there any solution of the fibrin, mere traces of proteïd being found in both liquids. If a ferment had been present in the blood, the fibrin in the second case would have entered into solution.

It therefore follows that the ferment had been produced by putrefactive bacteria in the first-described experiment. Such a ferment was, in fact, discovered in the undissolved residue; it was active in an alkaline solution, and was therefore of a nature of trypsin.

W. D. H.

Antiseptic Properties of Mercuric Cyanide, Oxycyanide, and Chloride. By CHIBRET (*Compt. rend.*, 107, 119—120).—Solutions of mercuric oxycyanide, $\text{HgO}, \text{Hg}(\text{CN})_2$, are feebly alkaline and give only a slight precipitate with solutions of albumin. They are much less irritating to living tissues than mercuric chloride, and a solution of 1 in 1500 has little action on ordinary metals. It is not decomposed by light. The oxycyanide was found to be six times as effective as the chloride in preserving cultivation liquids. A 1 per cent. solution of the oxycyanide, cyanide, or chloride kills *Micrococcus aureus* at once; a solution 1 : 1000 kills this organism in less than an hour, but a solution 1 : 3000 requires several hours. If agar-agar is immersed for three minutes in 1 : 3000 solution of any one of these salts, it will no longer grow *M. aureus*, and the effect persists for several days.

A solution of mercuric oxycyanide 1 : 1500 is much superior as an antiseptic to a solution of mercuric chloride.

C. H. B.

Tobacco and Bacteria. By V. TASSINARI (*Lancet*, 2, 1888, 729, from *Centr. Bakteriöl.*, 4, 15).—The germicidal virtues of tobacco-smoke were demonstrated by the use of the following apparatus:—In a chamber formed of two glass funnels placed horizontally and connected at their mouths by paraffin, is suspended from a loop of

platinum a small piece of linen, the lower end of which dips in a culture fluid containing the microbes. The chamber is connected at one end by a tube with a cigar or cigarette, and at the other by a tube containing a cotton-wool plug (to act as a filter) with the mouth of the experimenter. The smoke thus thoroughly surrounds the linen, and after the experiment, which lasts half an hour and involves the consumption of 3.5 to 4 grams of tobacco, the chamber is opened and the linen allowed to fall into a test-tube containing fluid gelatin. Seven varieties of pathogenic micro-organisms were thus examined, including those of cholera, anthrax, and pneumonia. In every instance there was very marked delay in the development of colonies in the gelatin compared with that of organisms dealt with similarly but without exposure to tobacco-smoke; and the development of some was entirely prevented. What substance or substances in the smoke have this action is to be the subject of renewed inquiry.

W. D. H.

Nitrification of Ammonium Salts. By H. LANDOLT (*Bied. Centr.*, 1888, 577—578).—In reply to Frank's criticisms of Plath's work (this vol., p. 521), the author, in conjunction with Plath, repeated the experiments of the latter and found:—(1) That after passing air through concentrated sulphuric acid and through aqueous soda, it gave no nitric or nitrous acid to pure aqueous soda solution even in 14 days; (2) that air thus purified when conducted over calcium carbonate for 14 days gave no trace of oxides of nitrogen; (3) that when the sterilised calcium carbonate was in contact with ammonium sulphate solution the result was the same. Two samples of soil were employed for the next experiments. After washing out with water the nitrates naturally present in the soils, they found that when left in contact with ammonium sulphate solution, nitrites and nitrates were formed when the soils had not been sterilised and were absent when sterilisation had been performed. In another experiment, they found that the natural amount of nitrates in the soils was not increased when they were left in contact with ammonium sulphate solution, having been previously sterilised by ignition and treated with water containing carbonic anhydride, and with phosphoric acid free from nitric acid, in order to neutralise the lime produced by the ignition. They, therefore, conclude that the inorganic constituents of the soil can effect no nitrification of ammonia.

H. H. R.

Growth of Maize and Peas in Nutritive Solutions. By E. HEIDEN (*Bied. Centr.*, 1888, 622—624).—At the Agricultural Exhibition at Bautzen, a set of experiments was arranged to illustrate the importance of the different plant foods. Maize and pea plants, in sets of five, were grown in nutritive solutions from which one or other of the foods were omitted; a set of each species was also grown in a solution containing all the plant foods. The average heights attained, expressed in centimetres, were as follows:—Lime absent, maize 18.9, peas 21; magnesia absent, maize 30, peas 44; nitrogen absent, maize 32, peas 51; phosphates absent, maize 24, peas 63; potash absent, maize 28, peas 45; all foods present, maize 100, peas 97. Both

species suffered most and died soonest when lime was absent. When iron was absent, the plants were pale, but grew for some time. The author could not get lupins to grow in nutritive solutions.

H. H. R.

Solid Hydrocarbons in Plants. By H. C. S. ABBOT and H. TRIMBLE (*Ber.*, 21, 2598—2599).—When *Cascara amarga* is extracted with light petroleum and the extracted substance crystallised from absolute alcohol, three distinct compounds are obtained. The one crystallises in silky needles, sometimes 2—4 cm. long, melts at $196.2\text{--}196.4^\circ$, and decomposes at a higher temperature; it dissolves in the usual solvents. When further purified, it contained 87.90 per cent. of carbon and 11.90 per cent. of hydrogen.

15 kilos. of *Phlox carolina* were extracted with light petroleum, and a hydrocarbon of the formula $(C_{11}H_{12})_x$ isolated.

N. H. M.

Galactose from Plum-Gum. By R. W. BAUER (*Landw. Versuchs-Stat.*, 1888, 214—215).—The gum (50 grams) was boiled for four hours with 200 c.c. of 55 per cent. sulphuric acid, filtered, neutralised with calcium carbonate, evaporated and extracted with absolute alcohol. In the residue, arabinose, dextrose, and galactose were found, the latter to the amount of 0.844 gram, having a rotatory power of $[\alpha]_D = 78.07$ at 12° in a tube 200 mm. long.

E. W. P.

Explanation of the Changes which the Nitrogenous Matters in Silage undergo. By E. SCHULZE (*Landw. Versuchs-Stat.*, 1888, 195—208).—After reviewing the researches of others in the same direction, the author draws this conclusion from their results, that in young plants which have been cut and kept moist in the dark, the albuminoids are converted into amides. He then details his own experiment with timothy grass and oats, when albuminoids decreased, but amides increased; in particular, asparagine was formed in very large quantity, although it was not present previous to siling. It appears that the extent of conversion is dependent on the character of the plants employed, and on the stage of growth at which the plants are cut, and that the asparagine, together with the other amides, may by the continued action of the fermenting organisms be further converted into ammonium salts and amido-acids (leucine, tyrosine, &c.). When then the silage is dried, dissociation of the ammoniacal salts occurs and ammonia is lost, and this accounts for the deficit of nitrogen which many have observed. If the plants have been previously dried before fermentation, no asparagine is formed at the expense of albuminoids, at any rate the proteids are but very slowly attacked; on the other hand, non-nitrogenous compounds are more readily attacked, and also the amides, consequently such silage must and does contain ammonia, and asparagine, &c., will be absent: these statements are all supported by analytical data. The loss of nitrogenous nutritive matter is therefore due to the formation of asparagine, &c., at the cost of albuminoids, and to the retardation of the action of the fermenting organisms, but which of the two causes has most influence is dependent on the character of the plant, and its period of growth and development when cut. The changes which

occur when sweet ensilage is made under pressure at 60° have still to be investigated. E. W. P.

Absorption of Nitrogen by Leguminosæ. By E. BRÉAL (*Compt. rend.*, 107, 397—399).—In several species of leguminosæ, the total nitrogen in the plant is about twice as great as that originally present in the seeds. If, however, the roots are covered with tubercular nodosities the amount of nitrogen is much greater. In one case with lucern it was 25 times as great as in the seed. These tubercles can be transferred from one plant to another by inoculation. They contain a whitish liquid full of microscopic, highly refractive, rounded granules, and moving filaments which resemble bacteria.

C. H. B.

Relation between Atmospheric Nitrogen and Vegetable Soils. By T. SCHLOESING (*Compt. rend.*, 107, 290—296).—In previous experiments (this vol., pp. 747 and 870), the oxygen and nitrogen were in contact with the soil in closed vessels without any communication with the outside air. Two new series of experiments were made, in one of which a slow current of air was passed continuously into the vessel containing the soils, whilst in the other the soils were freely exposed to the air. Seven varieties of soil were used, namely: (1) A very fertile alluvial mud from Boulogne-sur-Seine manured with dung and night soil; (2) its sub-soil from a depth of 0·6—0·7 m.; (3) a non-calcareous argillaceous sand from Neauphle; (4) its sub-soil at a depth of 0·4 to 0·5 m. (5, 6, 7), the soils from Grenelle, Fougilleuse, and Montretout respectively, used in the former experiments. All the soils were passed through a sieve and allowed to dry spontaneously before being analysed. The amount of moisture left in the soils varied from 13 to 18 per cent. The experiments extended from February, 1886, to April, and in some cases July, 1888. Nitrification went on as usual, and there was a decrease in the amount of ammonia. A small quantity of the carbon was converted into carbonic anhydride.

There was no appreciable difference between the total amount of nitrogen present in the soil at the end of the experiment and that originally existing in it. The differences were sometimes positive and sometimes negative, the maximum in each case being +0·53 and -0·57 milligram of nitrogen per 100 grams of soil. This result confirms the conclusion drawn from the previous series of experiments.

C. H. B.

Absorption of Nitrogen by Vegetable Soils and by Plants. By BERTHELOT (*Compt. rend.*, 107, 372—378).—In recent experiments which have given negative results, the soil has been treated merely as a chemical compound, without due regard to the bacteria which are present.

Three slightly calcareous argillaceous soils were used in the experiments described in this paper, two being somewhat rich in nitrogen, whilst the other contained only a very low proportion. In each soil, six species of leguminosæ (vetch, lupin, clover, lucern, &c.) were sown, and the experiments were made under four different conditions,

namely, with free exposure to air; under cover with free circulation of air; in closed vessels into which was passed each day 50 litres of filtered air free from ammonia and 1 litre of carbonic anhydride; in vessels hermetically sealed. Similar experiments were made with the same soils without living plants. The soil in each case was inoculated with bacteria which are supposed to be active in promoting the absorption of nitrogen. The experiments described relate to the series without plants and those with lupin and vetch, the latter being gathered when they reached maturity.

In all cases there was a distinct gain of nitrogen, the minimum being 0.083 gram or 2.1 per cent., and the maximum 0.9865 or 27.2 per cent. The soil growing no plants shows as well-marked an increase as soil with plants. With lupins, and with vetches in closed vessels, the gain of nitrogen takes place solely in the soil itself, the nitrogen in the plant being no greater than that in the seed, but in the case of vetches growing with free exposure to air, there is a very large increase of nitrogen and a considerable proportion of this is in the plant.

All these experiments were made with soils not very rich in nitrogen. With soils containing a large proportion of nitrogen, the increase is by no means so well marked, and in some cases there is even a decrease. With clover, any gain in nitrogen is almost entirely confined to the plant.

C. H. B.

Composition of Barleys grown in Württemberg in 1887. By BEHREND (*Bied. Centr.*, 1888, 620—622).—Saale barley and v. Trotha's Chevalier barley were grown and compared with local kinds of barley. Although the composition of the 89 samples examined varied very much, the starch ranging from 69.1 to 59.8 per cent., and the albuminoids from 8.1 to 11.7 per cent. (nitrogen from 1.30 to 1.37 per cent.), yet the average composition of the barleys of one kind did not differ from the averages given by the other kinds; hence the inference is drawn that the influence of soil, cultivation, &c., on the composition is so great that the influence due to the kind of seed may be neglected.

A classification of the barleys according to quality was made by experts, and on examining the composition of the samples in these classes, it appeared that the high class barleys were in the average the richest in starch and the poorest in albuminoids, and the low class barleys were just the reverse.

On placing the samples in groups containing about the same amount of starch, it was seen that the albuminoid averages for the groups were much about the same (10.0 to 10.3 per cent.) for those groups where the starch averages were not over 64.4 per cent., but for the groups with more starch than this, the albuminoid averages fell continuously as the starch averages rose.

H. H. R.

Egyptian Cigarettes. (*Lancet*, 2, 1888, 785—786).—This is the report of an analytical commission appointed to inquire into the alleged poisonous nature of Egyptian cigarettes. Five varieties were examined, and the results of analyses, microscopical and chemical, are

as follows:—The cigarettes are made of genuine tobacco and are free from opium. The ash contains a trace of copper which is probably due to the metallic lettering of the paper. Arsenic is absent.

Some proportion of Smyrna or Salouk tobacco is commonly incorporated with the Turkish, and this has an injurious action on the throats of some people, if it is present in excess. W. D. H.

The Composition of Stable Manure. By F. SESTINI (*Gazzetta*, 18, 44—54).—This paper contains the results of the analysis of a large number of samples of stable manure from the ox and from the horse, various kinds of litter being used. From the composition of these manures, the author considers that they are wanting in phosphoric acid rather than in potassium salts, and recommends the use in addition of artificial phosphatic manures. The nitrogen exceeds the 5 per cent. usually regarded as the theoretical amount necessary for a good manure, but it is not in a form in which it can be easily assimilated. C. E. G.

Lime and Ash in Tyrolese and other Wines. By E. MACH (*Bied. Centr.*, 1882, 638—640).—Determinations of lime and ash in a large number of wines.

Analytical Chemistry.

Instruments for Measuring Liquids. By GREINER and FRIEDRICH (Zeit. anal. Chem., 27, 470).—The authors have adapted the glass three-way cock with oblique perforations to a burette, which thus in one position of the plug is filled from below, and in the opposite position delivers its contents through a jet. For measuring out successive equal quantities of a liquid, the three-way cock is attached to a pipette made to contain the requisite volume when filled to overflowing. The liquid which overflows is caught in a funnel surrounding the stem of the pipette, and runs away through a side tube.

M. J. S.

Apparatus for Quantitative Analysis. By G. NEUMANN (J. pr. Chem. [2], 38, 85—91).—The author has improved his "hydrometer" (Abstr., 1887, 1140) by having a bulb of 100 c.c. capacity blown on the burette underneath the stop-cocked funnel. The stop-cock of the latter is three-way, so that connection may be made with a decomposing flask. A similar burette without bulb and stop-cocks is ground into the funnel, and quantities of gas smaller than 100 c.c. may be measured in this. The apparatus may be used as a Bunte's burette, as a Zulkowsky and Schiff's nitrogen measuring tube, and as a Lunge's nitrometer.

A funnel is described, having an air-tight cover with a cork and bent tube running through it, for the rapid washing of precipitates.

A dropping funnel with a three-way stop-cock, through which a gas as well as the liquid may be passed, and a peculiar litre flask, are also described. All are figured in the original paper. A. G. B.

Metallic Felt Filters. By C. E. MUNROE (*Chem. News*, 58, 101—102).—Ammonium platinochloride is placed while moist into a Gooch platinum crucible; the crucible is cleaned, dried, and carefully ignited; the resulting layer of platinum sponge forms a good filtering surface. If cracked, it may be repaired by applying some of the fresh salt to the crack and re-igniting. D. A. L.

Determination of Sulphur in Coke. By L. BLUM (*Zeit. anal. Chem.*, 27, 445—452).—Oxidation by wet reagents (hydrochloric acid and potassium chlorate, hydrochloric acid and bromine, aqua regia), although furnishing results which agree amongst themselves, in no case gives the whole of the sulphur present, but only a small proportion. The total sulphur is best determined by fusion; 1 part of the coke is fused with 4 parts of sodium carbonate, 8 parts of potassium nitrate, and 16 parts of sodium chloride. The mass is dissolved in hydrochloric acid, evaporated to dryness, redissolved in hydrochloric acid, filtered from silica, and the sulphuric acid then precipitated by barium chloride. In 10 samples of Belgian and Westphalian coke, the total sulphur ranged from 0.907 to 1.147 per cent. The sulphur found by wet oxidation is that present as metallic sulphides. The remainder, which exists as an organic compound, is, in the author's opinion, the more injurious of the two in metallurgical operations. M. J. S.

New Methods for Estimating Sulphur in Steel and in Iron for Steel-making. By J. O. ARNOLD and H. J. HARDY (*Chem. News*, 58, 41—44).—0.2 gram of the steel, a few pieces of pure stick zinc, and about 20 c.c. of water are placed in a flask of about 200 c.c. capacity, connected by means of two tubes and india-rubber joints with a graduated cylinder containing 1 : 4 sulphuric acid on one side, and with a tube marked at 30, 40, and 50 c.c. containing 30 c.c. of a solution of 25 grams of sodium hydroxide in a litre of water. The tube to the acid terminates at both ends with a fine aperture, whilst the end of the tube in the soda is also contracted. The water in the flask is boiled to expel air, the soda tube is then closed by clipping the india-rubber tube, and by removing the lamp 15 c.c. of acid is allowed to pass into the flask, when the india-rubber tube on the acid tube is also closed by clip. As soon as the pressure of hydrogen is sufficient, the soda tube clip is removed, and the gas is allowed to bubble through the soda, which absorbs all the hydrogen sulphide. The flask is heated until the steel is dissolved, when the acid continues to act on the zinc, the hydrogen driving the last portions of the hydrogen sulphide into the soda. The action is continued until the cooled contents in the soda tube measure 40 c.c., then 10 c.c. of a dilute acid solution of lead acetate is added, and the colour compared with a standard prepared at the time in a similar tube from pure lead acetate and hydrogen sulphide, from

which the amount of sulphur in the steel is calculated. The operation lasts less than half an hour, and with steels containing 0.01—0.04 of sulphur the results are within 0.01 per cent.; with 0.06—0.1 steels they are within 0.02 per cent., and with 0.11 to 0.14 steels within 0.03 per cent. Hence when good approximate results are required, the method answers well.

By another and somewhat more elaborate method results are obtained which are constant and accurate within less than 0.01 per cent. A flask supported on a sand-bath is connected with a reservoir of pure hydrogen and a series of 15 small tubes. The first acts simply as a condenser; the others contain each sufficient lead acetate solution (2 c.c. of a solution of 1.812 gram of crystallised normal lead acetate in 1000 c.c. of water acidified with acetic acid) to form lead sulphide with the hydrogen sulphide produced by 0.01 per cent. of sulphur in 2 grams of steel. This quantity of the metal is weighed into the flask, 30 c.c. of water is added, and the tube from the hydrogen reservoir just dips under it; 1 litre of hydrogen is aspirated through the apparatus to expel air, 30 c.c. of 1 : 4 sulphuric acid is added through a tap funnel, the whole carefully heated, and when the action is finished another litre of hydrogen is aspirated through, and the number of bottles discoloured is counted, and as no hydrogen sulphide passes out of a tube until all the lead is converted into sulphide, the number of discoloured tubes represents hundredths per cent. of sulphur in the steel. If the last tube is dark ruddy-brown, it may be considered as half the quantity, whilst a yellow-brown coloration indicates a trace of hydrogen sulphide. Neither copper nor phosphorus if present interfere with this process. The current of hydrogen drives all the hydrogen sulphide out of the first tube of the 15. D. A. L.

Estimation of Sulphur in Iron and Steel. By J. J. MORGAN and others (*Chem. News*, 58, 63, 70, and 95).—Morgan draws attention to weak points in various methods, but regards methods based on the oxidation to sulphuric acid by means of nitric acid as the most trustworthy; he nevertheless places great confidence in Parry's method (*Abstr.*, 1887, 1140). J. O. Arnold and H. J. Hardy do not, however, find the latter method capable of great accuracy, inasmuch as precipitation of lead sulphide occurs, which they attribute to the disturbance caused by the bubbling of the hydrogen sulphide into the liquid. B. W. Winder supports the views of the latter authors, commends their self-registering method (preceding Abstract), and refutes some of Morgan's experiments. D. A. L.

Sources of Error in Determinations of Nitrogen by Soda-lime, and Means for avoiding them. By W. O. ATWATER (*Amer. Chem. J.*, 10, 262—282; compare this vol., p. 990).—After reviewing the work of numerous analysts and describing his own experiments, the author concludes that there is no loss of ammonia either by dissociation or oxidation (1) if the tube is closely packed with soda-lime for a length of 12 cm., and this be heated before the distillation proper begins; (2) if the time of combustion is not more than three quarters of an hour; (3) if the tube is heated only to dull redness

and is allowed to cool somewhat before the last traces of ammonia are drawn out by a current of air. The insufficient mixing of the substance with soda-lime, the leaving of open channels above the mixture, protracted heating and employment of high temperatures, all tend to produce too low results. Kjeldahl's method is decidedly preferable for convenience, &c.; it is best, however, to check the two methods against one another, and with some substances it is necessary to control both by the absolute method. H. B.

Estimation of Nitrogen in Vegetable Soils. By BERTHELOT and G. ANDRÉ (*Compt. rend.*, 107, 207—209).—The estimation of nitrogen in soils presents some difficulty when part of the element is in the form of nitrates, and the various methods which have been devised for the estimation of the total nitrogen under these conditions are either difficult of execution or are liable to considerable errors.

The difficulty may be avoided in the case of true vegetable soils by treating them with four times their weight of cold water and thus removing the nitrates. This treatment removes at most a few milligrams of organic nitrogen per kilo., a quantity much smaller than the errors of the determination. C. H. B.

Estimation of Carbon and Nitrogen in Vegetable Soils. By T. SCHLOESING (*Compt. rend.*, 107, 296—301).—The ordinary method of combustion by means of oxygen and cupric oxide gives satisfactory results in the determination of the carbon in soils, but in order to avoid errors arising from the presence or formation of alkaline carbonates, the carbonates existing in the original soil and in the residue from the combustion should be carefully determined.

Nitrogen is most accurately estimated by Dumas' method, but the greatest care is required in sampling. In order to reduce the errors of experiment, the author operates on comparatively large quantities of soil. The combustion tube is 2 metres in length, and is drawn out at the end connected with the pump. This end of the tube is connected with a small distilling flask, in which the water is condensed, and the side tube of the flask is connected with the pump, the flask and joints being immersed in a beaker containing water. Commencing from the drawn-out end, the tube is filled with a layer of granulated cupric oxide 10 cm. in length, a layer of granular reduced copper 20 cm. in length, a second layer of cupric oxide 28 cm. long, and a tube, 2 cm. long, containing about 10 grams of pure lead carbonate, the different substances being separated by plugs of asbestos. The remainder of the tube, except about 15 cm. at the other end, is filled with the soil. The other end of the tube is connected with a retort containing pure potassium chlorate, the joint being surrounded by mercury.

The tube is made vacuous, the pump is stopped, and the potassium chlorate is heated until the gas in the tube is again at atmospheric pressure. A vacuum is again made, and the chlorate is heated gently in order to produce a slow current of oxygen. The lead carbonate is now heated until the gas issuing from the tube is completely absorbed by potash. The pump is then stopped, and the heating of the carbo-

nate continued until the tube is filled with carbonic anhydride at the ordinary pressure. The front part of the tube is now heated, and when the copper and copper oxide are red-hot, the soil is gradually heated. Destructive distillation of the organic matter takes place, and as soon as the soil is heated to redness, the potassium chlorate (which has been kept fused) is heated very carefully in order to obtain a regular stream of oxygen. As soon as combustion is complete, the tube is again made vacuous. The gas thus obtained is almost pure nitrogen, but sometimes contains a combustible gas amounting to 0.2 per cent., and occasionally even to 2 per cent. The presence of any nitric oxide is quite exceptional, and indeed was only observed in one instance. In the first stage of the combustion, the tube is filled with a reducing atmosphere, and it would seem that the gaseous oxygen is unable to oxidise the nitrogen during the subsequent combustion of the carbonised matter.

C. H. B.

The Azotometric Method of Soil Analysis. By A. BAUMANN (*Zeit. anal. Chem.*, 27, 457—461).—A rejoinder to Knop (this vol., 533). The author still maintains the uselessness of the azotometric method of determining the ammonia in soils, and recalls the experiments by which he showed that the contraction observed is due to humus, and is not prevented by the addition of even large quantities of borax solution.

M. J. S.

Estimation of Nitric Acid. By H. WILFARTH (*Zeit. anal. Chem.*, 27, 411—433).—In this modification of Schlösing's method the nitric oxide is absorbed by a mixture of sodium carbonate and hydrogen peroxide in presence of air. The apparatus consists of a flask in which the nitrate is boiled with ferrous chloride and hydrochloric acid. This is followed by a miniature Woulff's bottle for the condensation of the steam and the greater part of the hydrochloric acid. The gas next passes, through a Bunsen's caoutchouc valve, into a test-tube fitted as a washing bottle, and containing sodium carbonate, and thence to the absorption apparatus, which consists of a flask and a set of bulbs of peculiar form. The air is expelled from the decomposition flask by carbonic anhydride, which by means of a three-way cock can be diverted to the Woulff's bottle, and employed to drive back the condensed liquid into the decomposition flask. A branch tube serves for introducing the substance and reagents, and for removing the contents of the flask after the analysis. Not more than 0.5 gram of nitrate should be used. This is dissolved, and drawn into the flask, together with 20 c.c. of ferrous chloride (saturated solution), and 60 c.c. of hydrochloric acid (1.124), after filling the whole apparatus with carbonic anhydride. The absorption flask and bulbs are charged with a mixture of 20 c.c. of sodium carbonate solution (26 grams per litre), and 50 c.c. of hydrogen peroxide. The contents of the decomposition flask are boiled for five minutes, and then carbonic anhydride is passed for 10 to 15 minutes, a filter moistened with a solution of metadiamidobenzene being placed over the outlet of the bulb apparatus to detect any escape of nitrogen oxides. The soda-washing bottle is now disconnected from the absorption flask, and

the filter removed to that position to ascertain whether the last traces of nitric oxide have been swept out. When this is found to be the case, the absorption apparatus is set aside for an hour to complete the conversion of the nitrogen oxides into nitric acid. Its contents are then united; a measured excess of standard sulphuric acid is added; the mixture is boiled for 10 minutes, cooled, and the free acid (consisting of the nitric acid formed and the excess of sulphuric acid added) is titrated with soda (not baryta) solution, using an indicator (cochineal, litmus, lacmoid), not affected by the excess of hydrogen peroxide. Very satisfactory results have been obtained when using as little as 0.04 gram of potassium nitrate. Each determination occupies 25 to 30 minutes. M. J. S.

Phenol and some Allied Substances as Tests with Concentrated Sulphuric Acid for Nitrites, Nitrates, and Chlorates in Aqueous Solution. By D. LINDO (*Chem. News*, 58, 1—3, 15—17, 28—29).—The author employed the following solutions in his numerous experiments. Phenol:—10 c.c. of Calvert's No. 1 fused, dissolved in some water mixed with 25 c.c. of 97 per cent. alcohol, and made up to 100 c.c. with water. Orcinol:—5 grams dissolved in water, and made up to 100 c.c. Sulphuric acid, pure commercial, sp. gr. 1.837 at 26°. Nitric solution:—1.8723 grams of potassium nitrate made up to 100 c.c. = solution 100 N_2O_5 . Nitrous solution:—0.4053 gram of silver nitrite dissolved in 100 c.c. of boiling water, mixed with 0.160 gram of sodium chloride in solution, allowed to cool, made up to 200 c.c., agitated, and when settled and filtered = solution 2000 N_2O_3 . Chloric solution:—1.624 grams of potassium chlorate dissolved and made up to 100 c.c. = solution 100 Cl_2O_5 . The solutions of hydrochloric acid used were *a*, containing 26.16 per cent., *b*, 13.08 per cent., and *c*, 4.88 per cent. The sulphurous acid solution contained about 4 per cent. of the gas. The ferric chloride about 36.5 per cent. of the salt, the ferrous sulphate 10 per cent., and the copper sulphate 0.5 per cent. of the metal. In all experiments, 0.5 c.c. of the solution to be tested was mixed with one drop of phenol or two drops of orcinol solution, except with chlorates, when 1 drop of orcinol was employed; 2 c.c. of sulphuric acid is then run down the side of the tube so as to obtain bands of colour at the contact of the liquids. When sulphurous acid is used it is always added first, the phenol or orcinol being always the last added before the sulphuric acid. The following are some of the results obtained.

Phenol and nitrites:—A 200,000 N_2O_3 solution yields a faint pink band at first, faint green below; pink band very distinct in half an hour, but after five hours the colour has faded away. 50,000 N_2O_3 solution gives good red and green bands at once, fading after five hours. 2000 N_2O_3 solution very intense red and green bands in 24 hours, the latter changes to blue and the red to dingy purple. Solutions of intermediate strengths give intermediate reactions, and even 400,000 N_2O_3 gives a very faint band. Hydrochloric acid impedes or retards the reaction, so that 1 drop of solution *a* renders the colour with 200,000 N_2O_3 indistinct, and 2 drops upset the reaction with 50,000 N_2O_3 solution, and make the 10,000 give a light red band with

yellowish-green below. Two drops of sulphurous acid, on the other hand, prevent the colour forming even with the 2000 N_2O_5 solution; but with the addition of copper sulphate (see below) a slight pink band is obtained after two or three hours, presumably due to a trace of N_2O_5 .

Orcinol and nitrites:—One of nitrite in 1,000,000 of water gives a faint but uncertain indication after some time; 500,000 N_2O_5 gives a very faint pink after four hours, becoming more distinct in nine hours; 10,000 N_2O_5 solution gives a strong orange band at once, becoming almost opaque after some time. The colour is permanent. Hydrochloric and sulphurous acids both interfere with the reaction, but copper sulphate with hydrochloric acid increases the delicacy; 1,000,000 N_2O_5 + 1 drop of copper sulphate + 2 drops of orcinol + hydrochloric acid, sharp orange-pink band in 10 minutes.

Phenol and nitrates:—No reaction with 1 N_2O_5 in 20,000 of water. 10,000 N_2O_5 faint, pink band becoming broader and less definite, ultimately fading; 1000 N_2O_5 , intense red band, pale green below becoming very dense. Intermediate and stronger reactions are given in the original. Phenol alone appears to be but a poor test for nitrates, but in the presence of hydrochloric acid it becomes very delicate; by adding one drop of solution c 100,000 N_2O_5 gives a faint pink at once, which becomes distinct in 20 minutes, spreads and ultimately fades; 10,000 N_2O_5 , a sharp, crimson band at once, spreading without losing intensity for some hours, and faint green below, soon fading. 1000 N_2O_5 , very dense red, green below. Sulphurous acid does not interfere with this test, or with the corresponding one with orcinol. Neither ferric chloride nor copper sulphate disturbs this reaction, in fact, the latter rather improves it with highly dilute N_2O_5 solutions; but ferrous sulphate is fatal, so that with 1 drop of the solution, and hydrochloric acid 10,000 N_2O_5 gives no reaction, and 5000 is very indistinct.

Orcinol and nitrates:—The remarks which apply to phenol are mostly true of orcinol, but with the addition of hydrochloric acid the latter is more sensitive, indicating by a faint pink colour 1 N_2O_5 in 200,000 in three hours, and with extreme faintness 1 in 500,000. The colour is permanent, and orcinol may be regarded as very superior to phenol for detecting traces of nitrate in the presence of large quantities of hydrochloric acid or chlorides. Ferric chloride is objectionable, but neither sulphurous acid nor ferrous sulphate interferes with the reaction, whilst copper sulphate makes it more delicate; 500,000 N_2O_5 with hydrochloric acid, 1 drop of copper solution and 2 drops of orcinol gives sharp bands in five minutes.

With chlorates, phenol gives a pale yellow band with blue below, the latter soon fading with 10,000 Cl_2O_5 ; with 4000, the blue soon changes to dingy green, with 2000 the blue is dingy and becomes dingy green; with 1000 and upwards no blue is developed. Orcinol is somewhat more delicate, 100,000 Cl_2O_5 giving a faint transient blue band, which becomes more distinct as the strength of the solution increases, so that with 10,000 Cl_2O_5 a beautiful blue band is produced, soon acquiring the colours of the rainbow, 4000 gives a similar effect, but not so good, owing to interference of a deep green coloration: 1000 gives an intense green, soon turning brown, and 100 only a pale yellow. These changes are not observed with other oxidising agents, and therefore this may possibly

become a characteristic test for chloric acid. Hydrochloric and sulphurous acids interfere slightly with this reaction.

These reactions have been applied to the detection of nitrites, nitrates, and chlorates in the presence of each other, and the author has tested this point by various mixtures made from his solutions. With nitrites and nitrates in various proportions there seems to be no difficulty in detecting them both; the nitrite is first identified, the mixture is then treated with a drop or two of sulphurous acid to destroy the nitrite; to ensure the complete destruction of the nitrite the solution of the mixture should be acid; it is then tested again with hydrochloric acid and orcinol, or if great delicacy is desired, with the addition of copper sulphate, when mere traces of nitrate give a coloration. With nitrites and chlorates, the red coloration with phenol and sulphuric acid due to nitrites is first obtained; and then, after treatment with sulphurous acid, the chlorate may be detected by the blue colour with orcinol and sulphuric acid. The results show that chlorate can be detected when mixed with a considerable excess of nitrite after the latter has been destroyed with sulphurous acid, but nitrites cannot be detected by this method if the chlorate is greatly in excess. With mixtures of chlorates and nitrates, the former cannot be detected if the latter are in considerable excess; but, on the other hand, a small quantity of nitrate can be detected in the presence of a large quantity of chlorate, since by allowing the sulphurous acid to act for about 15 minutes the chlorate is completely destroyed, whilst the nitrate remains and gives its colour reaction in the usual manner; when, however, the chlorate is not in great excess the nitrate may even be detected with hydrochloric acid, phenol, and sulphuric acid, without previously destroying the chlorate. When all three are present in the same solution, they can be tested by these reactions only when the proportions indicated above are not exceeded; for instance, a mixture of equal volumes of 10,000 N_2O_3 , 10,000 N_2O_5 , and 10,000 Cl_2O_7 , would give the red band with phenol and sulphuric acid for nitrites; a blue band with 1 drop of sulphurous acid and 1 drop of orcinol for chlorates; and by treatment with 2 drops of sulphurous acid and 1 drop of hydrochloric acid, allowing to remain 15 minutes, copper sulphate and orcinol would give the orange bands due to nitrate.

The presence of iodides, bromides, and even chlorides in large quantities would prevent the detection of nitrites, nitrates, or chlorates by this method, if these are present, therefore, the solution must be precipitated with silver sulphate. Thymol and α -naphthol do not give distinct and characteristic reactions for these salts under the conditions given in the paper; but the following test is recommended by the author for nitrite in very dilute solutions: two or three drops of the alcoholic α -naphthol and one or two drops of 1:1 sulphuric acid added to 10 c.c. of 1 in 1,000,000 nitrite solution, gives in a few minutes a pale, greenish-yellow colour; with much stronger solutions, a precipitate separates, and the colour of the liquid approaches orange.

For the sake of comparison, the following substances were tested with sulphuric acid and 1 drop of phenol or 1 drop of orcinol to 0.5 c.c. of the solution:—Potassium ferricyanide in strong solution gave a brown band with sulphuric acid alone, in weak solutions it gave a brown band

with phenol, and yellow turning brown with orcinol. $\frac{N}{50}$ Potassium permanganate gave with *phenol* a broad, turbid, light reddish-brown band; and with *hydrochloric acid*, in addition, a broad, pale yellow upper band with a narrow, ruddy lower band, changing to bright vermilion; with *orcinol*, it gave reddish upper and dull green lower band, and with *hydrochloric acid* in addition a dull orange upper and emerald-green lower band; in presence of two drops of sulphurous acid, no reaction. Potassium dichromate, 0.5 gram per litre of water, with or without hydrochloric acid, gave with *phenol* a brown band soon becoming lighter, with *orcinol*, a dull, prismatic band; in presence of sulphurous acid no reaction: distinction from chlorates. Hydrogen peroxide, 3 vols. strength diluted with 20 vols. of water, gave with *phenol* a reddish upper, and dull green lower band, and with *hydrochloric acid* a very faint, purple band, changing to pink; with *orcinol*, a sharp reddish band, changing to dull orange above, olive-green below, and with *hydrochloric acid* a purple upper, weak olive-green lower band; no reaction in presence of sulphurous acid.

The above reactions refer only to dilute solutions as indicated in the paper; very different results would be obtained with either stronger reagents or stronger solutions. The average temperature throughout these experiments was about 26°.

The following is a convenient reagent for detecting nitrites or nitrates:—Dissolve 2.5 grams of orcinol in a mixture consisting of 25 c.c. of 2 per cent. copper sulphate solution, 1 c.c. of pure sulphuric acid, and 25 c.c. of pure 15 per cent. hydrochloric acid, and filter; 2 drops of this are added to 0.5 c.c. of the solution to be tested, and 2 c.c. of sulphuric acid run in. If the reaction, as already described above, occurs in presence of sulphurous acid, nitrates are present. (See also next Abstract.)

D. A. L.

Griess' Sulphanilic Acid Test for Nitrous Acid modified.

By D. LINDO (*Chem. News*, 58, 40).—The author has made experiments with thymol, orcinol, and α -naphthol as well as with phenol; he confirms Gambelli's results as regards colour and the advantage of making the solution alkaline (*Abstr.*, 1887, 533). He takes 5 c.c. of nitrite solution, adds 1 drop of a saturated solution of sulphanilic acid in 1 : 5 sulphuric acid, 1 drop of phenol or thymol, and after 10 minutes mixes well with 1 c.c. of ammonia. Thymol gives an orange-yellow not so defined as phenol. The limit of this method, using 5 c.c. of solution, is 1 part of N_2O_3 in 10,000,000 of water. The author suggests the use of the method in the reverse order as a test for phenols. Orcinol gives as good a reaction as phenol, but becomes coloured of itself on exposure to the air in presence of alkali, and is therefore untrustworthy.

D. A. L.

Qualitative Test for Phosphoric Acid of Mineral Origin, in presence of Phosphoric Acid of Animal Origin in Artificial Manures. By N. V. LORENZ (*Chem. Centr.*, 1888, 1039).—The test depends on the fact that mineral phosphates all contain much more fluorine than bones. 30 grams of the manure are treated in a beaker with 15 c.c. of concentrated sulphuric acid and covered with a watch-

glass, on the underside of which is a drop of water. The silicon fluoride evolved in the case of a mineral phosphate, causes a deposition of silica in the drop of water. J. W. L.

Volumetric Estimation of Phosphoric Acid by means of Molybdic Acid. By A. GRETE (*Ber.*, 21, 2762—2765).—Phosphoric acid can be estimated volumetrically as follows:—A known quantity of the solution is neutralised, using methyl-orange as indicator, and any precipitate which may be produced, dissolved by a few drops of nitric acid. An equal volume of a 75 per cent. solution of ammonium nitrate, about 1 gram of sodium sulphate, and 1 c.c. of a solution of gelatin are added, the whole heated at about 80—90°, and titrated with a solution of ammonium molybdate until no further precipitation occurs. The mixture is constantly shaken during titration, and from time to time a little of the gelatin solution is added as long as it produces a precipitate. When the titration is almost completed, the solution is heated and stirred until the precipitate becomes granular; the end of the reaction is then easily observed. If too much molybdate has been run in, a few cubic centimetres of phosphoric acid can be added and the solution again titrated.

The molybdate solution is prepared by mixing 1 kilo. of ammonium molybdate, dissolved in ammoniacal water, with 100 grams of gelatin which has been previously boiled for some time with dilute nitric acid and pouring the slightly alkaline, yellow liquid into about 3 litres of concentrated nitric acid (sp. gr. 1.2). The mixture is diluted to 10 litres, kept for several days with frequent shaking, filtered, and standardised.

The gelatin solution is prepared by boiling 100 grams of gelatin with water and about 50 c.c. of nitric acid, and diluting to 1 litre. A few cubic centimetres of this solution suffice for the precipitation of 0.1 gram P_2O_5 .

The analysis can be carried out in 20 to 30 minutes, and the results are very satisfactory. F. S. K.

Determination of Carbon in Iron. By L. L. DE KONINCK (*Zeit. anal. Chem.*, 27, 463—464).—In the process in which the iron is dissolved by a mixture of cupric and ammonium chlorides (Creath) and the residue oxidised by sulphuric and chromic acids (Ullgren), it is necessary to wash the chlorides out of the residue very completely, otherwise chlorine will be evolved with the carbonic anhydride. The addition of an excess of silver sulphate to the mixture in the oxidation flask obviates this difficulty, not a trace of chlorine being evolved. M. J. S.

Polaristrobometric Analysis of a Mixture of Sodium and Potassium Chlorides. By F. SCHÜTT (*Ber.*, 21, 2586—2594).—The method of analysis which is based on the influence of inactive compounds on the rotation of polarising substances, forms a ready means of determining the relative amounts of sodium and potassium in solutions from which other substances have already been separated.

The metals are converted into chlorides, and 10 grams of the well-dried mixture put into a Mohr's 50 c.c. flask; 11 grams of potassium

tartrate (with $\frac{1}{2}$ mol. H_2O) previously dried at 110° is then added. the whole dissolved in warm water, cooled to 20° , and the flask filled exactly to the mark. It is well shaken and filtered quickly; the filtrate is then polarised in a 400 mm. tube at 29° . The rotation is first determined with pure sodium chloride and potassium tartrate (22 grams of NaCl , 22 grams of $\text{C}_4\text{H}_4\text{K}_2\text{O}_6 + \frac{1}{2}\text{H}_2\text{O}$ dissolved to 100 c.c.), then with pure potassium chloride, and the difference calculated. Tables are given by means of which the percentage of potassium can be found after the rotation has been determined; also a table showing actual percentage amounts of potassium chloride and the amounts as determined (from 5 to 95 per cent.); the greatest error is ± 0.5 .

N. H. M.

Estimation of Lithium as Fluoride. By A. CARNOT (*Compt. rend.*, 107, 237—240).—Freshly precipitated lithium fluoride requires for complete solution at the ordinary temperature 800 parts of pure water and 1900 parts of a mixture of equal volumes of water and ammonia solution. In presence of a small quantity of ammonium fluoride, the solubility is still further reduced, probably because the dissociation of the lithium fluoride is prevented, and solution of the precipitate requires 2100 parts of water, 3000 parts of a mixture of 3 vols. water and 1 vol. ammonia solution, and 3500 parts of a mixture of equal volumes of water and ammonia. Sodium fluoride requires 70 parts of the last mixture for complete solution, but the potassium, caesium, and rubidium compounds are much more soluble.

The ammonium fluoride required is purified by boiling it for a short time with twice its volume of ammonia solution, filtering off the precipitated silica, and preserving the concentrated ammoniacal solution.

The solution containing, say, a few decigrams of a lithium salt with not more than 10 or 15 times its weight of other alkaline salts, is concentrated to a few c.c., mixed with 15 to 20 c.c. of ammonium fluoride and ammonia, and allowed to remain overnight. The precipitate is washed two or three times with a few c.c. of water containing ammonium fluoride and ammonia, dried, heated to expel excess of ammonium fluoride, mixed with excess of sulphuric acid, and the lithium weighed as sulphate. The volume of the filtrate and the washings should be measured. Since part of the liquid is in contact with the precipitate for a short time only, it may be taken that 10 c.c. contains 2 mgrms. of lithium fluoride, approximately equivalent to 4 mgrms. of the sulphate. The examples given are very satisfactory.

C. H. B.

Estimation of Lithium in Mineral Waters. By A. CARNOT (*Compt. rend.*, 107, 336—339).—From 1 to 10 litres of the water is concentrated by evaporation, and the compounds of iron, magnesium, barium, calcium, strontium, and ammonium, and the silica, carbonic acid, and sulphuric acid are removed by the usual methods. The residue, which consists of alkaline chlorides with probably a small quantity of magnesium chloride, is evaporated to dryness, the liquid being well stirred towards the end of the operation in order to obtain a granular residue. This residue is extracted with alcohol of 90 per

cent., the alcohol distilled off, and the residue evaporated with water acidified with hydrochloric acid, and, whilst still moist, treated with concentrated alcohol, and finally with alcohol and ether. The alcoholic solution is evaporated to dryness, the residue dissolved in 15 to 20 c.c. of water, and treated with ammonium fluoride in the manner already described (preceding Abstract). The lithium fluoride is dried and weighed, and then converted into sulphate and again weighed. This affords a valuable check on the result, since the weight of the sulphate is almost exactly double that of the fluoride, whilst in the case of potassium and sodium the ratio is very different. Should the relation between the two weights indicate that the lithium salt is not pure, it should be redissolved in water and the precipitation repeated.

In order to separate small quantities of magnesium, the sulphate is dissolved in 40 to 50 c.c. of water, and heated with ammonia and sodium phosphate.

In calculating the quantity of lithium dissolved from the fluoride by the washings, 7 c.c. and not 10 c.c. as stated in the previous paper (*loc. cit.*), contain 2 mgrms. of lithium fluoride.

A spring at Maizières, which contained 3.644 grams of solid matter per litre, contained 0.0240 grams of lithium oxide, whilst another at Sautenay contained 8.980 grams of solid matter and 0.0310 of lithium oxide.

C. H. B.

Use of Hydroxylamine Hydrochloride in Quantitative Analysis. By A. LAINER (*Monatsh.*, 9, 533—536).—The author finds that silver nitrate and halogen silver compounds, either in the solid condition or dissolved in sodium thiosulphate or potassium cyanide, are perfectly reduced by treatment with hydroxylamine hydrochloride and alkali. The reduced silver can be readily transferred to a filter and weighed. Results of analyses are given showing the accuracy of the method.

G. T. M.

Estimation and Separation of Zinc. By J. RIBAN (*Compt. rend.*, 107, 341—343).—The solution is mixed with sodium carbonate until a slight, permanent precipitate is formed, and this is redissolved by addition of a small quantity of hydrochloric acid. An excess of a slightly acid solution of sodium or barium dithionate is added, the liquid diluted so that 100 c.c. contain not more than 0.1 gram of zinc, and it is then saturated with hydrogen sulphide in the cold. Under these conditions, zinc sulphide separates as a very dense, granular precipitate, which is readily washed with warm water containing hydrogen sulphide. If the solution is sufficiently dilute, the liberated dithionic acid exerts no appreciable solvent action on the precipitate.

This method is available for the separation of zinc from manganese, iron, and other metals which are not precipitated by hydrogen sulphide in presence of dithionic acid.

C. H. B.

Copper Assays. By J. W. WESTMORELAND (*Chem. News*, 58, 76—79).—The author does not approve of the fire assay or of the cyanide method; he also disagrees with Peter's strong advocacy of the electrolytic method inasmuch as silver, bismuth, lead, arsenic, tin,

manganese and ferric salts all interfere with it. He advocates E. O. Brown's iodine process, titrating in an acetic acid solution. (Compare Abstr., 1887, 80.) D. A. L.

Detection of Mercury in Urine by Electrolysis. By ZIEGLER (*Chem. Centr.*, 1888, 1040, from *Monatsh. pr. Dermatologie*, **7**, 557—558).—150 c.c. of urine is warmed with 1.5 grams of potassium permanganate. When the oxidation is complete, the liquid is filtered and 100 c.c. is treated with 5 grams of sulphuric acid, the liquid shaken to expel carbonic anhydride, and the further examination conducted according to Wolf's method (*Chem. Centr.*, 1888, 867).

J. W. L.

The Electrolytic Method as applied to Iron. By E. F. SMITH (*Amer. Chem. J.*, **10**, 330—332).—The solution is mixed with an excess of sodium citrate and a little free citric acid; using about 70 to 150 c.c. of liquid and a current liberating 6 c.c. oxhydrogen gas per minute; the deposition generally takes four hours. The separation is complete, the metal is compact, regular, and steel-like, and after washing successively with water, alcohol, and ether, and drying it does not alter when exposed to the air. The presence of aluminium or of titanium does not interfere. A number of test analyses are given.

H. B.

Separation of Arsenic, Antimony, and Tin from Gold and Platinum. By L. L. DE KONINCK and A. LECREMIER (*Zeit. anal. Chem.*, **27**, 462—463).—The precipitated sulphides are heated in a stream of hydrogen chloride. Antimony and tin volatilise as chlorides, arsenic as sulphide: gold and platinum remain.

M. J. S.

Bromine for Gold Extraction. By W. H. BURFEIND (*Chem. News*, **58**, 92).—The use of bromine is suggested as a substitute for chlorine in the laboratory and perhaps in the works also; for the extraction of gold, it has the advantage of requiring no generating apparatus. A weighed quantity of the ore is washed, put in a bottle with bromine-water, agitated from time to time, more bromine added, if required, until there is still an excess of bromine after an hour or so. The precipitate is well washed and the filtrate is treated in the same manner as if chlorine had been used.

D. A. L.

Determination of Oxygen in Water. By BLAREZ (*J. Pharm.* [5], **18**, 55—58).—An estimation can be made in 10 minutes. The following titrated solutions are required:—Sodium hydroxide, one equivalent per litre; ferrous ammonium sulphate, 40 grams per litre, slightly acidified with sulphuric acid; sulphuric acid diluted with an equal volume of water; decinormal solution of potassium permanganate. The apparatus employed is a bromine tube with a bulb capacity of about 250 c.c., the tube of which is cut off 2 to 3 cm. below the stop-cock. Above the bulb is a caoutchouc stopper carrying a cylindrical funnel of about 12 c.c. capacity, having a capillary tube terminating level with the underside of the stopper. The capacity of the tube is measured by filling with water up to the middle of the neck which receives the

stopper and running out the water into a graduated tube; this is only required once for each apparatus. 30 to 35 c.c. of mercury is measured accurately and poured into the tube; 10 c.c. of normal sodium hydroxide is now added and the water to be examined is run in up to the mark in the neck; the volume of water taken is thus known. The stopper with funnel is now thrust into the neck so as to remove all the air; a little water may rise into the funnel, a little mercury run out at the stopcock brings the level down to the bottom of the stopper. Exactly 5 c.c. of the ferrous solution is now placed in the funnel and carefully passed into the tube by running out more mercury until the level of the liquid is again brought to the bottom of the stopper. The liquids are now mixed by giving the tube a gyratory movement, and in five or six minutes the oxygen may be considered to be completely absorbed. There is now added 10 c.c. of sulphuric acid in the same way as the ferrous solution; on agitating the tube, the contents become clear at once. The mercury is now run out, and the aqueous contents are poured out and titrated with permanganate solution. J. T.

Estimation of Glycerol in Crude Glycerin. By R. BENEDIKT and M. CANTOR (*Monatsh.*, 9, 521—527).—From 1 to $1\frac{1}{2}$ grams of the sample is heated for from 1 to $1\frac{1}{2}$ hours with from $\frac{7}{2}$ to 8 grams of acetic anhydride and about 3 grams of anhydrous sodium acetate, in a wide-mouthed 100 c.c. flask provided with a reflux condenser. After cooling, 50 c.c. of water is added, the flask is again attached to the condenser, and the contents are heated just to the boiling point. By this operation, the glycerol is quantitatively converted into triacetin. The solution is filtered and the amount of triacetin present determined by means of standard caustic soda and hydrochloric acid. Di- and tri-glycerides are decomposed by acetic anhydride in an almost precisely similar way. G. T. M.

Estimation of Glycerol by Oxidation. By V. PLANCHON (*Compt. rend.*, 107, 246—247).—When a solution of glycerol is mixed with potassium permanganate and sulphuric acid, there is no appreciable action in the cold, but at 40° carbonic anhydride is evolved, and at a higher temperature oxidation proceeds rapidly and regularly. The carbon is completely converted into carbonic anhydride, and by absorbing this gas in soda-lime, the quantity of glycerol can be accurately estimated. C. H. B.

Determination of Cane-sugar in Liqueurs, Confectionery, and Chocolate. By F. RATHGEN (*Zeit. anal. Chem.*, 27, 433—445).—This may be effected by the use of the saccharimeter. The chief difficulties lie in the preparation of perfectly clear solutions, and in the presence of other optically active substances. Turbid solutions may generally be clarified by shaking with alumina, which has been precipitated from the sulphate by ammonia and thoroughly washed. In the case of chocolate, the further addition of lead acetate and alum is necessary. Coloured liquids should be shaken with blood charcoal. In the absence of inverted sugar or glucose (which may

be known by the absence of reduction when the solution is warmed with copper sulphate and soda), a simple reading (A) in the polariscope, gives by the usual formula the percentage of cane-sugar, but since part of the sugar is generally found to have been inverted by the action of the fruit acids, it is necessary to complete the inversion by heating a portion of the liquid with hydrochloric acid and then to make a second observation, B. If the amount of substance proper to the instrument in use has been taken, the formula $\frac{100(A-B)}{42.4-0.5t}$, gives the

percentage of cane-sugar at the time of analysis, and $\frac{100 B}{42.4-0.5t}$, the

original percentage. Since the amount of rotation produced by invert sugar is affected by the presence of alcohol, it is necessary in examining liqueurs to evaporate (after neutralising with ammonia) and make up with water. Ammonia should also be added when extracting the sugar from such articles as candied fruits, jellies, and syrups, in all of which much of the sugar will be found to be inverted. The results are given of the examination of numerous liqueurs and articles of confectionery.

M. J. S.

Detection of Aldehyde. By W. WINDISCH (*Zeit. anal. Chem.*, **27**, 514; *Zeit. für Spirit. Ind.*, **9**, 519; *Chem. Zeitung*, **11**, 24).—With metaphenylenediamine hydrochloride, aldehyde forms a reddish-brown, resinous substance, soluble in water and alcohol with blood-red colour and green fluorescence. Highly dilute solutions (1 of aldehyde in 200,000) give a yellow colour, which disappears on treatment with an alkali, and is restored by addition of hydrochloric acid.

M. J. S.

Acetone in Urine. By LEGAL (*J. Pharm.* [5], **18**, 206—207, from *J. Méd. Paris*).—To detect acetone in urine, add some drops of a concentrated solution of sodium nitroprusside, and make the mixture alkaline by the addition of a little potassium hydroxide. A red coloration is produced which disappears after some time; when this has taken place, a little acetic acid is added, and, if acetone is present in the urine, a deep-violet coloration appears. Acetone is found in diabetic urine. Ferric chloride is employed to detect ethyl acetoacetate in urine; in this case, the urine becomes deep-red. The urine of patients who have taken thalline, antipyrine, salicylic acid, and phenol gives the same reaction with ferric chloride, but the colour disappears on boiling in the case of ethyl acetoacetate. If the urine be previously boiled, the colour is not produced in the latter case, but is produced with the other substances.

J. T.

Valuation of Crude Sodium Acetate. By G. NEUMANN (*J. pr. Chem.* [2], **38**, 91—97).—This is a modification of Phillips's method (*Abstr.*, 1886, 747). The dropping funnel has a three-way cock, so that a stream of air may be passed through the apparatus; the air is supplied through a T-piece, so that when it is turned off by the three-way cock it may be used to force the liquid through the funnel, thus preventing the escape by upward pressure from the retort.

The carbonic anhydride is estimated at the same time by connect-

ing the receiver with weighed absorption tubes. The carbonaceous matter in the residue from the distillation is determined by combustion with chromic and sulphuric acids in Classen's apparatus.

A. G. B.

Estimation of Hydrogen Potassium Tartrate and Free Tartaric Acid in Wines. By B. HAAS (*Chem. Centr.*, 1888, 1045—1046, from *Zeit. Nahr. Hygiene*, 2, 97—100).—Two quantities of 50 c.c. each of the wines are evaporated in dishes on the water-bath to about 4 c.c. One of these is, previously to the concentration, half neutralised with potassium carbonate. After the desired concentration is effected, 2 c.c. of glacial acetic acid is added to the half-neutralised portion for each gram of neutralised tartaric acid. 100 c.c. of 95 per cent. alcohol is added to each portion, and the hydrogen potassium tartrate is collected and titrated with alkali. The difference between the amounts of hydrogen tartrate as thus determined corresponds with the free tartaric acid in the wine.

J. W. L.

Test for Uric Acid. By G. DENIGÈS (*J. Pharm.* [5], 18, 161—162).—The reaction depends on the transformation of uric acid into alloxanic products under the action of nitric acid or of bromine-water, the solution of these compounds in concentrated sulphuric acid, and on the blue colour communicated to commercial benzene by this solution. A little uric acid is placed in a small porcelain capsule with two drops of water and one or two drops of nitric acid, the whole is gently evaporated to dryness, when the mass should be still yellow, or scarcely reddish. It is dissolved in two or three drops of concentrated sulphuric acid, and on adding commercial benzene a beautiful blue coloration appears. The coloration is due to the action of thiophen contained in the benzene obtained from coal-tar on the alloxan and other alloxanic compounds, resulting from the oxidation of uric acid by nitric acid or bromine-water.

J. T.

Determination of Fat in Milk, Cream, &c. By C. SCHMID (*Zeit. anal. Chem.*, 27, 464).—In a test-tube of about 50 c.c. capacity, graduated in tenths of a cubic centimetre, 5 c.c. of cream or 10 c.c. of milk is placed; 10 c.c. of concentrated hydrochloric acid is added, and the mixture is boiled with shaking until it becomes dark brown. After cooling, 30 c.c. of ether is added, and the tube is well shaken. The ethereal and aqueous layers separate perfectly clear. The volume of the former is read, and 10 c.c. withdrawn by a pipette is evaporated in a tared basin on the water-bath, whilst blowing upon its surface. The fat is dried at 100° and weighed, and the amount calculated for the whole of the ether solution. The entire operation takes about a quarter of an hour, and gives results of the highest accuracy.

M. J. S.

Analysis of Butter, Oleomargarin, &c. By H. N. MORSE and W. M. BURTON (*Amer. Chem. J.*, 10, 322—328).—Hehner's and Koettstorfer's methods of analysis are not capable of distinguishing between good butter and mixtures of butter with certain fats. The following method, which may be made very simple, discriminates in

such cases very easily, and depends on the determination of the total fatty acids, and of those soluble and of those insoluble in water. The following numbers, expressing the percentage of alkali required to neutralise (a) the insoluble and (b) soluble acids respectively, show the great difference between butter and other fats and oils:—Butter, (a) 86·57, (b) 13·17; cocoanut-oil, (a) 91·95, (b) 8·17; ditto washed with water, (a) 92·43, (b) 7·42; ditto washed with dilute sodium carbonate solution, (a) 92·33, (b) 7·45; cotton-seed oil, (a) 92·05, (b) 7·76; oleomargarin, (a) 95·40, (b) 4·57; lard, (a) 95·96, (b) 3·82; beef tallow, (a) 96·72, (b) 3·40. The fat is melted, filtered, and well stirred during solidification; a sample is then saponified with a measured quantity of alcoholic potash, and the excess of the latter determined by hydrochloric acid and phenolphthaleïn; the total acids are thus found. The alcoholic solution is evaporated to dryness and the soap treated with exactly enough hydrochloric acid to liberate all the fatty acids; the liquids are heated in a flask fitted with a reflux condenser until the oil has separated, when it is filtered, and the two sets of acids thus separated are then easily estimated.

H. B.

Action of Sulphur Chloride on Oils, &c. By T. T. P. B. WARREN (*Chem. News*, 58, 4, 15).—Although genuine lard and lard oil yield products with sulphur chloride which are perfectly soluble in carbon bisulphide, yet mixtures of equal parts of cotton-seed oil and lard oil do not, as might be expected, yield a product containing 50 per cent. soluble, in fact, some of the lard oil product appears to be retained by the altered cotton oil. The author now finds that cotton oil does not dissolve when boiled even with concentrated potash; therefore to overcome difficulties like that just noted, the mixed product is saponified with 30 per cent. potash, the glycerol is determined and the fatty acids examined; in this manner, a clue is obtained as to the character of the oils present which yield solid products soluble in carbon bisulphide, but are retained by the insoluble mass. Cases may occur where sulphur chloride yields an insoluble product, but that owing to its solubility in an accompanying soluble fat the insoluble substance may be overlooked; in such cases, a saponification test will also be found useful, as for instance, when cotton oil and lard fat are mixed in such proportions as to yield a soluble sulphur chloride product. The author has succeeded in reproducing cotton oil by heating a mixture of the acids obtained from cotton oil and glycerol in a sealed tube at about 260°, for several weeks; he hence confirms Berthelot's observation on this point; it is noteworthy that the cotton oil acids, unlike the oil, yield with sulphur chloride products soluble in carbon bisulphide. The author points out that the stability of the fatty glycerides in different oils is intimately connected with the drying properties; and the iodine absorption of an oil before and after exposure to the air in a warm place gives an idea of the change effected during oxidation; for example, the iodine absorption of poppy oil exposed in an open dish at 60° fell from 135 to 119 per cent. in 10 days, a sample of rape oil under similar conditions was much bleached, but its iodine absorption only fell 10 per cent. The author attributes

the dark hue of the sulphur chloride products from oxidised oils to the loss of glycerol.

In examining olive oil adulterated with lard and poppy oil, the author determines the total iodine absorption of the mixture, the lard oil is then removed by boiling with moderately strong alkali, supplemented if necessary by washing with ether, then having ascertained the iodine absorption due to the lard oil, it is not difficult to fix on the mixture of olive and poppy oil which yields the residual iodine absorption; the reduction of the iodine absorption of poppy oil by oxidation is an element of uncertainty. The presence of poppy oil may be confirmed by passing ozone through the mixture for a short time; the sulphur chloride product being black and more viscid if it is present.

D. A. L.

Detection of Sesame Oil in Olive Oil. By E. MILLAU (*J. Pharm.* [5], 18, 169—170, from *Monit.-sci.*, 1888).—On treating olive oil directly with sugared hydrochloric acid, a rose colour may be obtained with a perfectly pure oil. Various experiments have shown that the colour in this case is due to the aqueous portion which passes from the fruit pulp when the oil is extracted by pressure. Consequently, to test olive oil for sesame oil, it is necessary to remove this aqueous portion by heating at 110°; then a portion treated with an equal volume of sugared hydrochloric acid in a test-tube gives a rose colour if any sesame oil is present, but remains absolutely colourless if pure.

J. T.

Detection of Cotton-seed Oil in Olive Oil. By E. MILLAU (*J. Pharm.* [5], 18, 170—171, from *Monit.-sci.*, 1888).—In a porcelain basin of 1000 c.c. capacity, 15 c.c. of the oil in question is heated to about 110°, then, still continuing the heat, a mixture of 15 c.c. of sodium hydroxide of 40° B. and 15 c.c. of alcohol of 92° is slowly poured on to the oil. When the mass becomes homogeneous, 500 c.c. of water is added drop by drop so as to avoid cooling the mass and the formation of lumps. After boiling a short time, the fatty acids are separated by dilute (one-tenth) sulphuric acid. When the acid is in slight excess, about 5 c.c. of the fatty acids is heated gently on the water-bath with 20 c.c. of alcohol to solution, 2 c.c. of silver nitrate solution (30 grams to 100 c.c. water) is added, and the heating continued until about one-third of the liquid has evaporated. The fatty acid remains unchanged if the oil is pure; but if cotton-seed oil is present metallic silver is precipitated. The reaction is very sensitive, indicating 1 per cent. of cotton-seed oil. Sources of error are avoided by thus working on the fatty acids separated by the process.

J. T.

Determination of the Oil in Linseed Cake. By R. KLOPSCH (*Zeit. anal. Chem.*, 27, 452—457).—It is necessary that the cake intended for extraction with ether should not be dried at too high a temperature or for too long a time. Three hours in the water-oven (at 94—96°) is sufficient to dry the sample thoroughly, and has no influence on the oil determination, but after six hours at that

temperature, and still more markedly at a higher temperature (105°), considerably less oil is extracted by ether. The cause of this is under investigation.

M. J. S.

Estimation of Mustard Oil in Seeds of Cruciferae. By O. FÖRSTER (*Landw. Versuchs-Stat.*, 1888, 209—214).—As the various methods heretofore in use for the estimation of mustard oil in seeds are more or less incorrect, the following method has been devised, and used with good results: 25 grams of the powdered substance (oil cake) is made into a thin paste with water, allowed to remain for half an hour, and then heated by the introduction of steam, whereby the oil is volatilised; and may be collected by the usual arrangements of condenser, &c., in a 250 c.c. flask containing 50 c.c. ammoniacal alcohol; when about 150 c.c. of liquid has distilled over, the liquid is allowed to remain for 12 hours in a closed vessel, and afterwards brought to boiling in a beaker, and freshly prepared mercuric oxide is added, sufficient to combine with all the sulphur present. The mixture is then again boiled, and before it is quite cold potassium cyanide is added to remove all excess of mercuric oxide and oxydimercurammonium hydroxide; the weight of the mercuric sulphide obtained is then multiplied by 0.4266, the product representing the mustard oil. The mercuric oxide employed is prepared by decomposing 25 c.c. of a 4 per cent. solution of mercuric chloride with potassium hydroxide and boiling the mixture. A small loss may occur due to the formation of the mustard oil, since potassium myronate in presence of myrosin and water yields besides mustard oil, small quantities of crotonitrile and free sulphur, which remain in the retort; the extent to which this may occur can be estimated by preliminary experiments; sinapolin (diallylcarbamide) carbonic anhydride, and sulphuretted hydrogen may be formed, or diallylthiocarbamide may be produced, but in both cases the hydrogen sulphide simultaneously formed combines with the mustard oil, producing allylamine and carbon bisulphide, or diallylthiocarbamide and carbon bisulphide; the sulphur is not lost, as with alcoholic ammonia it forms ammonium thiocarbonate, which yields mercuric sulphide with mercuric oxide.

E. W. P.

Tests for Antipyrine and Antifebrine, and Fahlberg's "Saccharin." By D. LINDO (*Chem. News*, 58, 51).—The author suggests the following reaction as a test for "saccharin." Not less than 0.5 mgrm. solid "saccharin" is evaporated to dryness over a water-bath with excess of nitric acid, and whilst still on the bath, a piece of potash and a few drops of water, or better still, of 50 per cent. alcohol are added; colour develops immediately, and by inclining the dish streaks of blue, violet, purple, and red flow from the potash.

Antipyrine is heated with concentrated nitric acid over a flame until reaction commences, the flame being then removed. When the action ceases, a fine purple liquid remains, which on adding water and filtering yields a purple-red solution and a violet precipitate.

A minute quantity of antifebrine is strongly heated with a little pure concentrated sulphuric acid, the product when cool is mixed with

water and with some highly dilute nitrite solution, and may then be tested like ordinary sulphanilic acid by means of γ -naphthol, thymol, or phenol.

D. A. L.

Estimation of Emetine. By A. KREMEL (*Arch. Pharm.* [3], **26**, 419, from *Pharm. Post.* **21**, 151).—10 grams of ipecacuanha root, finely powdered, is rubbed up with the same amount of potassium hydroxide and water, dried on a water-bath, finely powdered, and extracted with hot chloroform. After evaporation of the nearly colourless solution, the emetine, which is slightly yellow, is dried at 100° and weighed. The average amount obtained is 1.80 per cent. Flückiger's method, extraction with ammoniacal chloroform, does not yield the emetine sufficiently pure to give the value of the ipecacuanha root.

J. T.

Filtering "Crude Fibre" and Silver Chloride. By T. B. OSBORNE (*Chem. News*, **58**, 90—91).—The following plan of filtration is suggested as rapid and efficient for crude fibre determinations. Fold the paper to form a cone of somewhat smaller angle than that of the funnel, place in position on the platinum cone, moisten and apply suction; the paper generally tears down a fold, forming a narrow rift from vertex upwards with a loose network of fibres across it. The liquid and fibre to be filtered are stirred up and thrown on this filter; filtration proceeds rapidly and well.

When there is any difficulty in filtering silver chloride from solutions containing organic matter, the greater part of the liquid should be passed through a Gooch filter, the precipitate should then be dissolved in slight excess of ammonia, reprecipitated with nitric acid, and washed by decantation; it can then be thrown on the filter without fear of passing through.

D. A. L.

ERRATA.

VOL. XLVI.

Page Line
748 20 from bottom for "C. Fischer" read "O. Fischer."

VOL. XLVIII.

744	17	"	top	}	"	" isosaccharic acid "	read	" isosaccharinic acid."
"	9	"	bottom					
"	26	"	top					
745	9	"	"	}	"	" isosaccharate "	"	" isosaccharinate."
"	18	"	"					
"	14	"	"					
1013	10	"	bottom	}	"	" creasote "	"	" creosote."
1342	col. ii, 21	"	"					
1078	18	"	top					
		"	"		"	" Hantsch "	"	" Hantzsch."

VOL. L.

631	9	"	bottom	"	" Ber., 9 "	"	" Ber., 19."
1012	17	"	top	"	" 585 "	"	" 885."
1013	col. ii, 17	"	bottom	"	" 1040 "	"	" 1014."
1033	14	"	"	"	" orthotolylaniline "	"	" orthotolylaniline."

VOL. LII.

139	6	"	"	"	$\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \begin{array}{c} \text{N} \\ \\ \text{NH} \end{array} \text{C}_6\text{H}_2\text{Me} \cdot \text{NH}_2$	read	$\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{array}{c} \text{C}_6\text{H}_2\text{Me}(\text{NH}_2) \\ \text{NH} \end{array} > .$
437	20	"	"	"	"Ann. Chim. Phys."	read	"Ann. Phys. Chem."
651	12	"	"	"	"C ₁₅ H ₁₆ NO ₄ "	"	"C ₁₅ H ₁₆ N ₄ O."
727	3	"	top	"	"Hentzschel"	"	"Hantzsch."
737	2	"	bottom	"	"Valem"	"	"Valeur."
738	21	"	top	"	"carbamide"	"	"carbamine."
976	6	"	bottom	"	"methylketone"	"	"methylketole."
1070	20	"	"	"	"Günwald"	"	"Grünwald."

ERRATA.

VOL. LIV.

Page	Line			
34	19	from bottom	for	"H. SAUER" read "A. SAUER."
39	13	" top	"	"β-phenylacrosazones" read "-phenylacrosazones."
46	12	" bottom	"	"mannite" "mannitol."
67	3	" "	"	"Abstr., 1882, 92" "Abstr., 1883, 92."
123	20	" "	"	"S. A. PRIBYTEK" "S. PRIBYTEK."
154	3	" top	"	"Diphthalic acid" "Diphthalic acid."
188	top line	" "	"	"N. REALI" "N. REALE."
248	7	" "	"	"fatty nitroketones" read "the hydrogen sodium sulphite compounds of fatty nitrosoketones."
267	13	" bottom	"	"sugar" "sugars."
294	5	" top	"	"T. BOUCHARDAT" "G. BOUCHARDAT."
357	9	" "	"	"A. MAASEN" "A. MAASEN."
379	23	" "	"	"Quinine alkaloids" "Cinchona alkaloids."
388	24	" "	"	"nitric acid" "nitric oxide."
415	13	" "	"	"H. W. WARREN" "H. N. WARREN."
424	23	" "	"	"Trans., 1886, 379" "Trans., 1886, 708."
426	1 & 4	" "	"	"Platoso-" "Platino-."
429	21	" bottom	"	"H. TAUFs" "H. TAUSs."
456	19	" top	"	"A. MOSso" "U. MOSso."
466	17	" "	"	"Isobutylphenylenediamine" read "Isobutylphenylenediamine."
483	12 & 13	" bottom	"	"skatole" read "scatole."
492	8	" "	"	"OH·C ₆ H ₂ Me< $\begin{smallmatrix} \text{CO} \\ \text{CH} \end{smallmatrix}$ >C ₆ H ₃ ·OH"
				read "OH·C ₆ H ₂ Me< $\begin{smallmatrix} \text{CO} \\ \text{CH}_2 \end{smallmatrix}$ >C ₆ H ₃ ·OH."
493	13	" "	"	"triacetyl" read "tetracetyl."
557	20	" "	"	"R. WAGNER" "R. F. WAGNER."
617	14	" top	"	"J. ROSENHEIM" "T. ROSENHEIM."
646	16	" bottom	"	"CLANDON" "CLAUDON."
679	10	" top	"	"Mononaphthene" "Nononaphthene."
693	2	" bottom	"	"S. RACINE" "(?) S. RAEINE."
745	23	" top	"	"secretion" "aëration."
761	22	" "	"	"29-30°" "20-30°."
775	11	" "	"	"NADESCHIDIN" "NADESCHDIN."
827	22	" "	"	"hexabenzoiç" "hexazobenzoiç."
834	15	" "	"	"A. SCHEUK" "A. SCHENCK."
894	12	" bottom	"	"T. GERLACH" "G. T. GERLACH."
916	26	" top	"	"R. G. GRISSON" "R. G. GR·SSOM."
924	16	" "	"	"C. HERSH" "C. HERSCH."
971	14	" "	"	"1883" "1885."
1005	9	" "	"	"37" "31."
1103	7	" bottom	"	"JACCKLE" "JAECKLE."
1035	16	" top	"	"MeO" "MgO."
1051	22 & 26	" "	"	"hexamethylene" "hexamethylenamine."
1067	21	" bottom	"	"Ethylmalonate" "Ethyl Malonate."
1128	14	" "	"	"Berques" "Bergues."
1141	4	" "	"	"coils" "cells."
1203	26	" top	"	"Dihydrazanthraquinone" read "Dihydroxyanthraquinone."